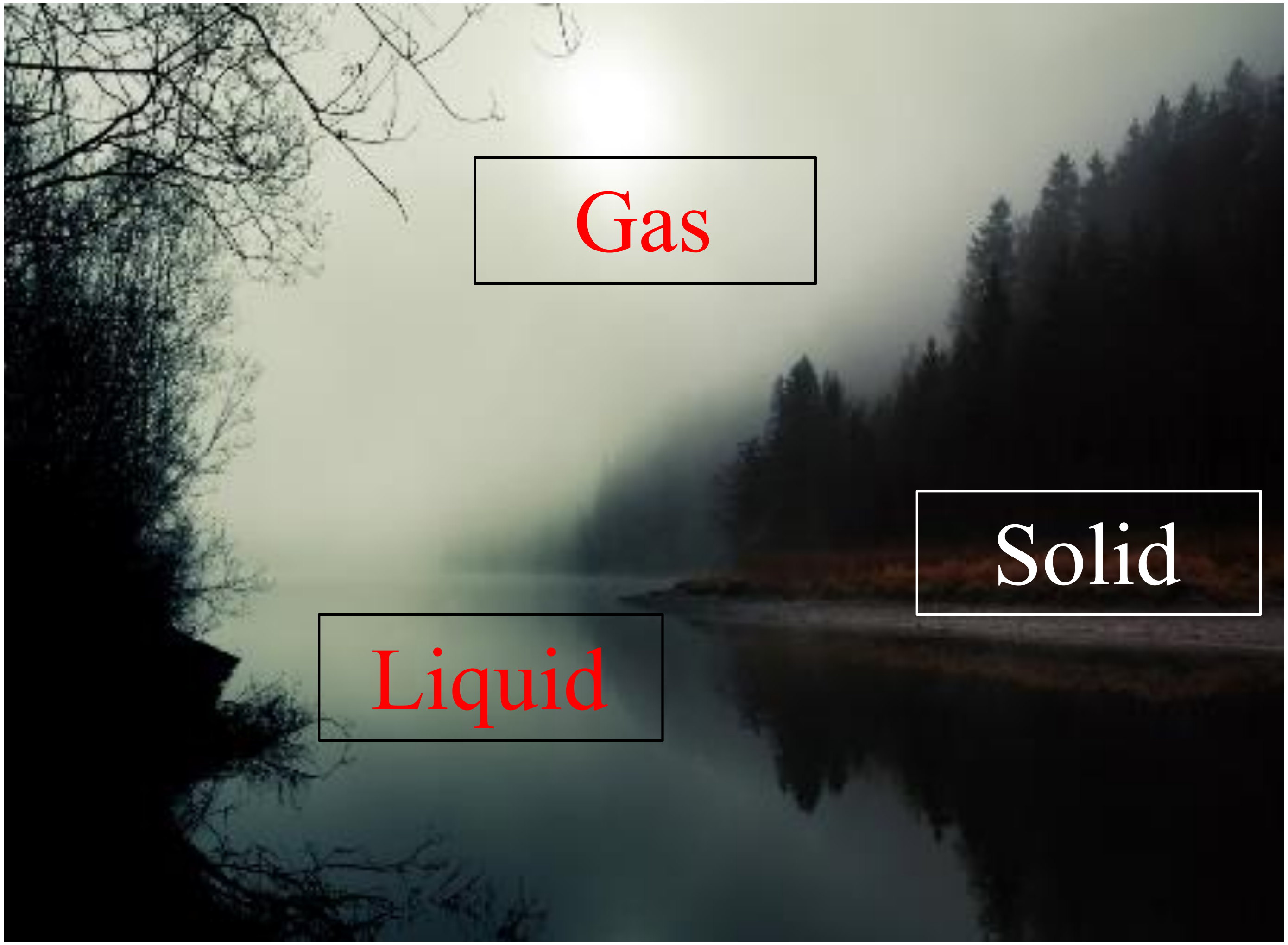
Non-equilibrium Kinetics of the Transformation of Liquids into Physical Gels

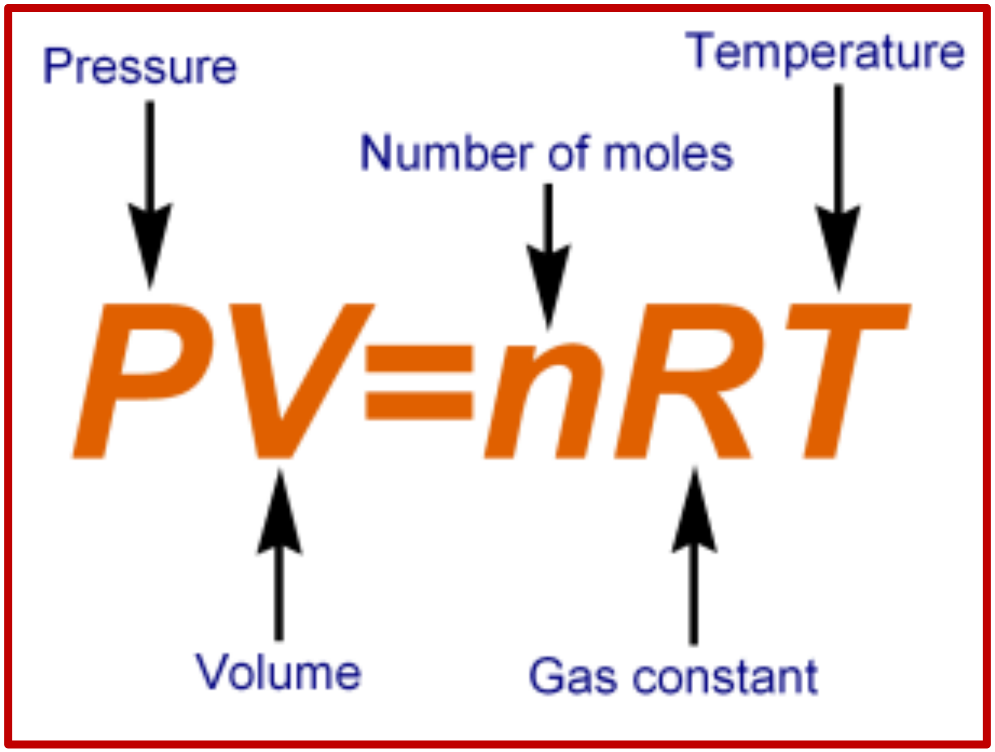
M. Medina Noyola
Instituto de Física "Manuel Sandoval Vallarta"
Universidad Autónoma de San Luis Potosí

ENTROPY, INFORMATION AND ORDER IN SOFT MATTER
ICTS Bangalore, September 2018.

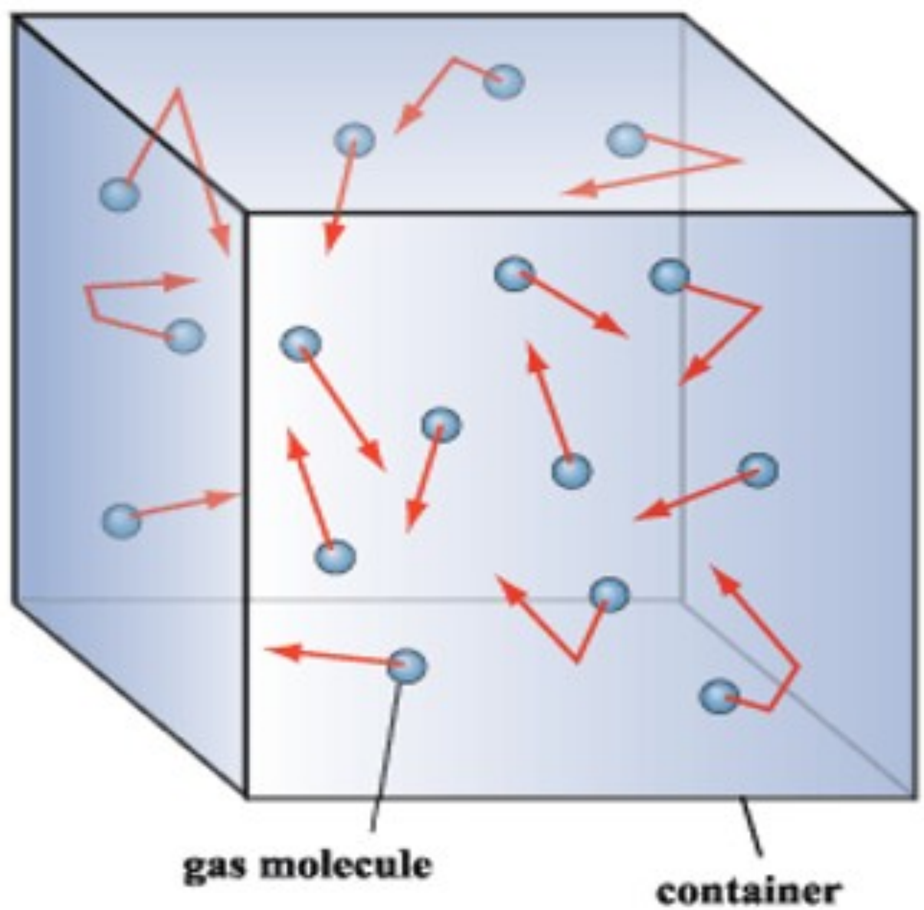
Understanding the States of Matter



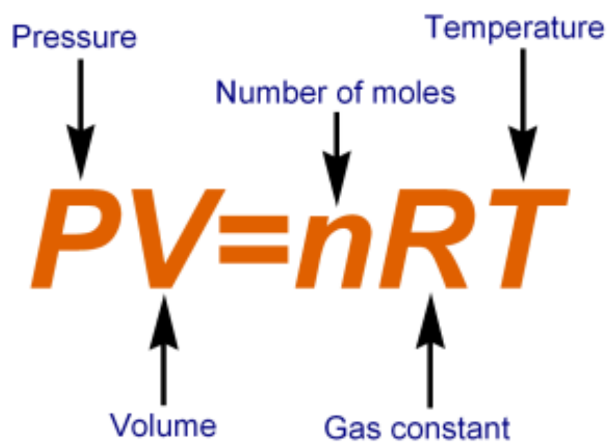
Characterizing the States of Matter



Understanding = in Molecular Terms



Understanding = in Molecular Terms



STATISTICAL THERMODYNAMICS: UNIVERSAL PRINCIPLES

Termodinámica Clásica (Callen)

PRIMERA LEY: $\mathbf{A}=[A_1 , A_2 ,\dots, A_M]$.

(Y la energía interna es una de ellas.)

Termodinámica Clásica (Callen)

SEGUNDA LEY: Relación Termodinámica Fundamental:

$$S = S[\mathbf{A}]$$

StatisticalThermodynamics

u(r)

$$S[\mathbf{A}]=k_B\, \mathit{Log}\ W[\mathbf{A}]$$

Ecuaciones de Estado

Diagramas de Fase de Equilibrio

FOR EQUILIBRIUM, MANY FORMATS TO PLAY BOLTZMANN'S GAME!

StatisticalThermodynamics

u(r)

MINIMIZING FREE ENERGY

Ecuaciones de Estado

Diagramas de Fase de Equilibrio

StatisticalThermodynamics

u(r)

DENSITY FUNCTIONAL THEORY

Ecuaciones de Estado

Diagramas de Fase de Equilibrio

StatisticalThermodynamics

u(r)

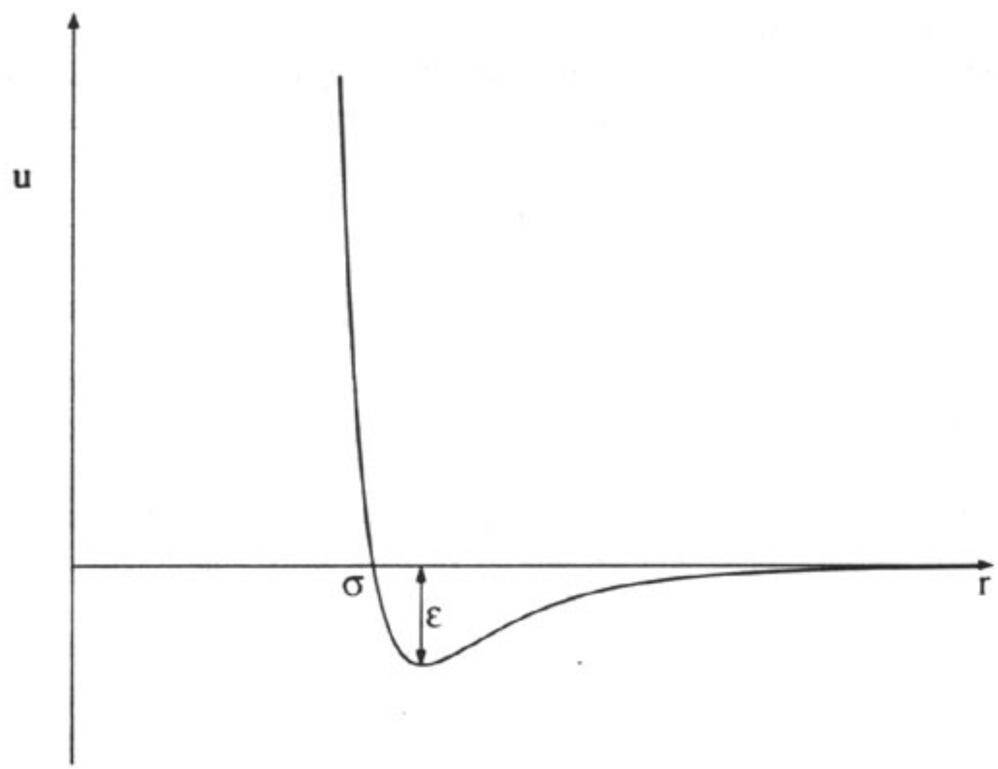
MONTECARLO SIMULATIONS

Ecuaciones de Estado

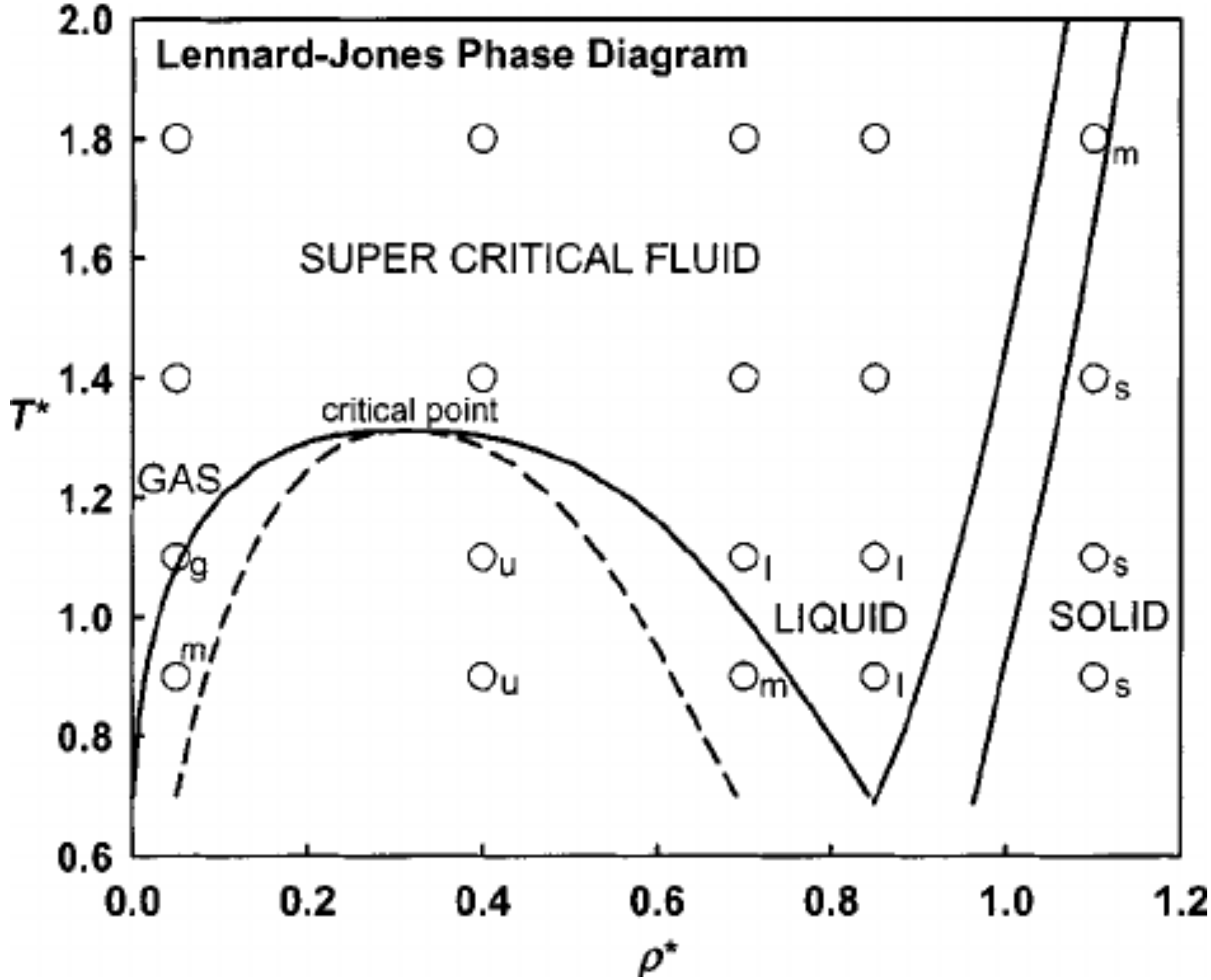
Diagramas de Fase de Equilibrio

LENNARD-JONES POTENTIAL

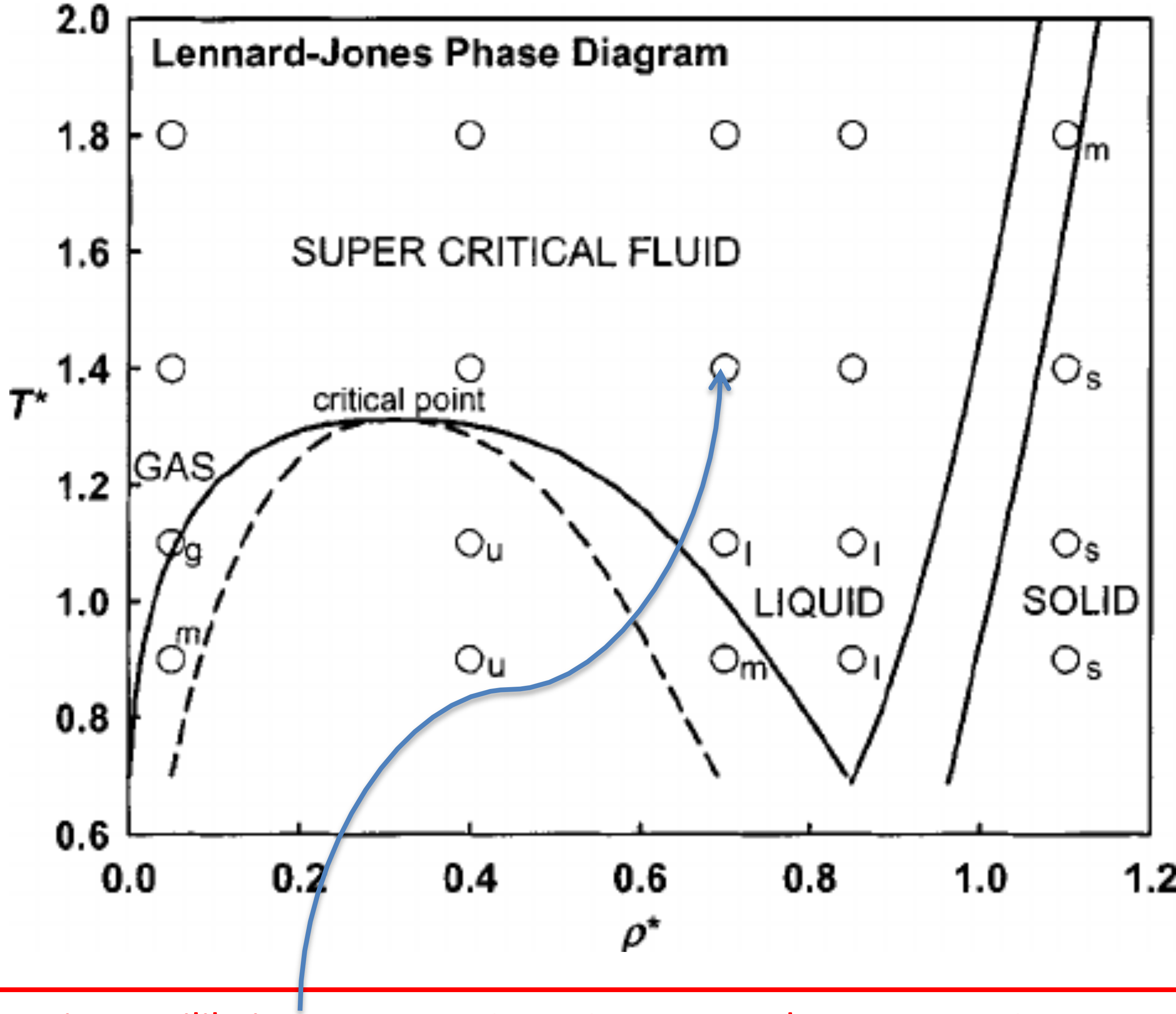
$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Equilibrium Phase Diagram

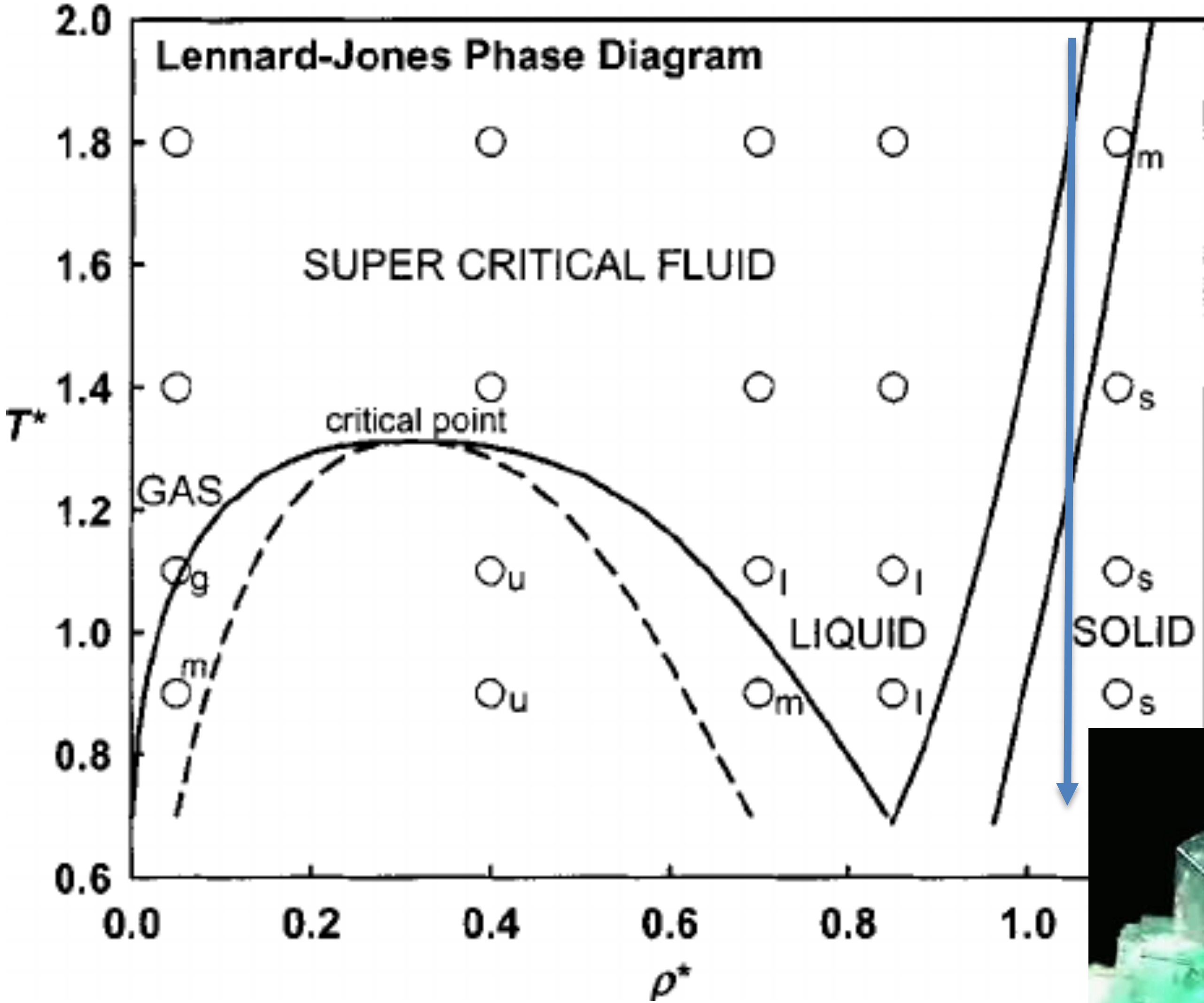


Equilibrium Phase Diagram

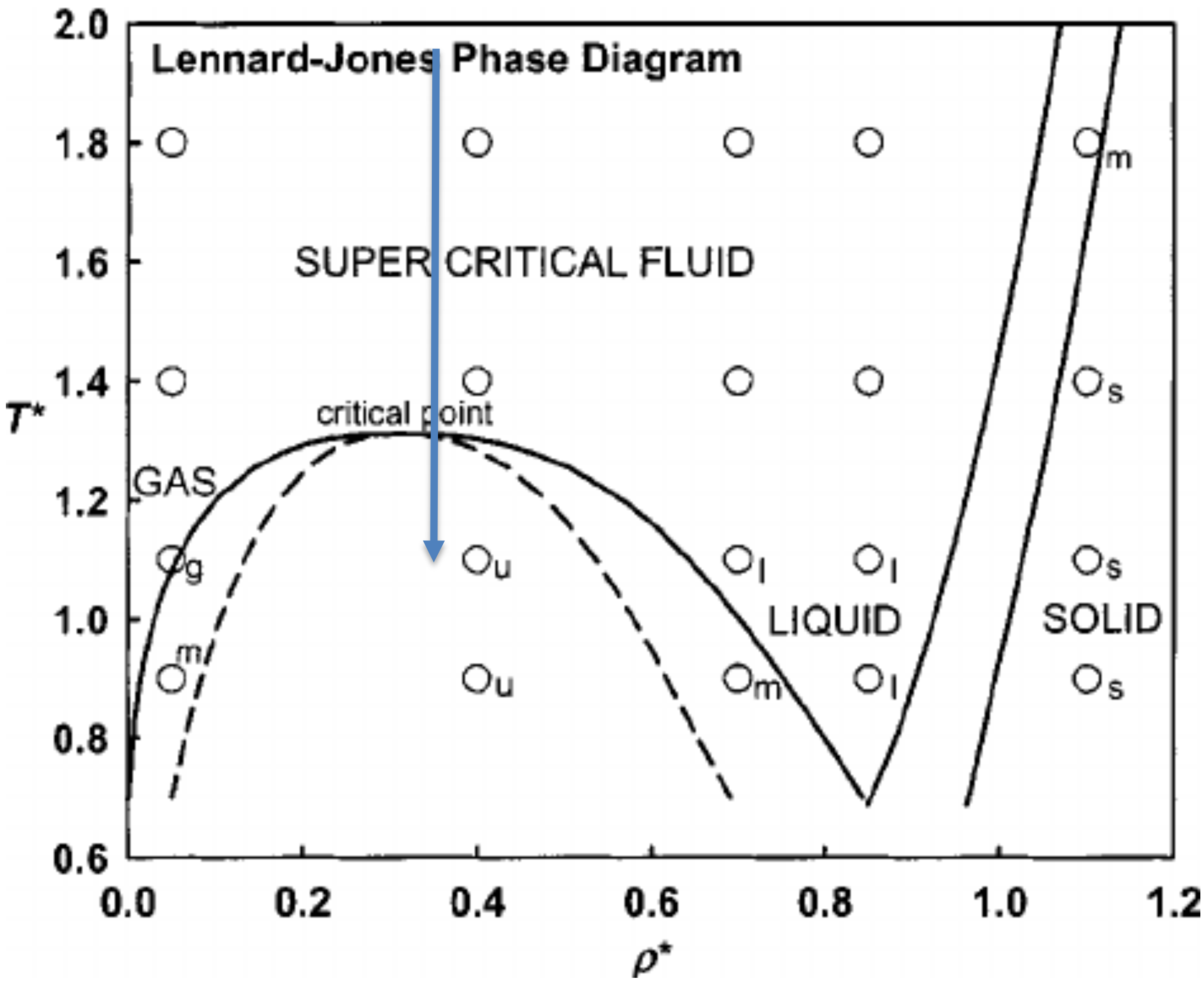


Thermodynamic equilibrium states : STATIONARY and PREPARATION-INDEPENDENT

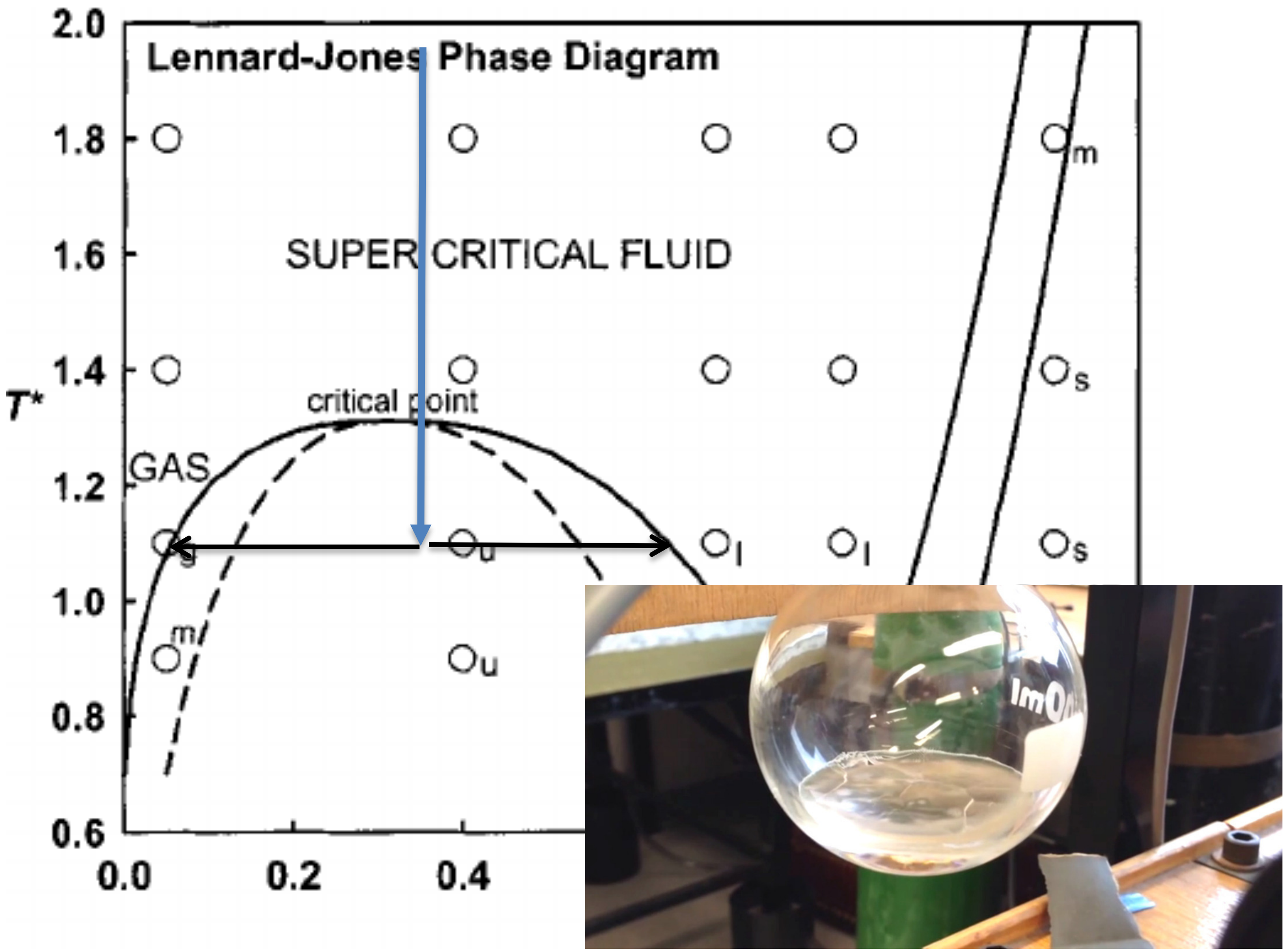
Equilibrium Phase Diagram



Equilibrium Phase Diagram



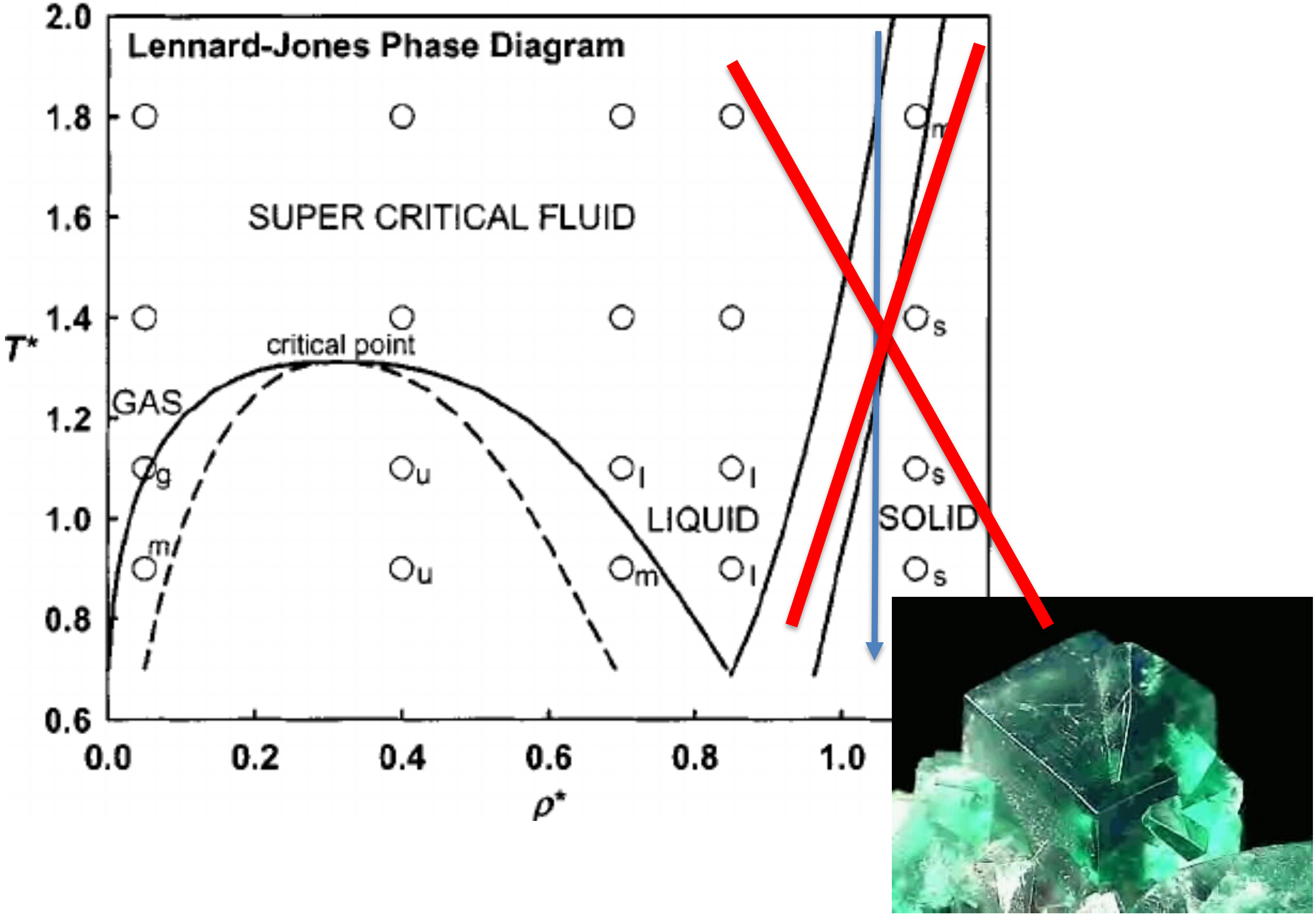
Equilibrium Phase Diagram



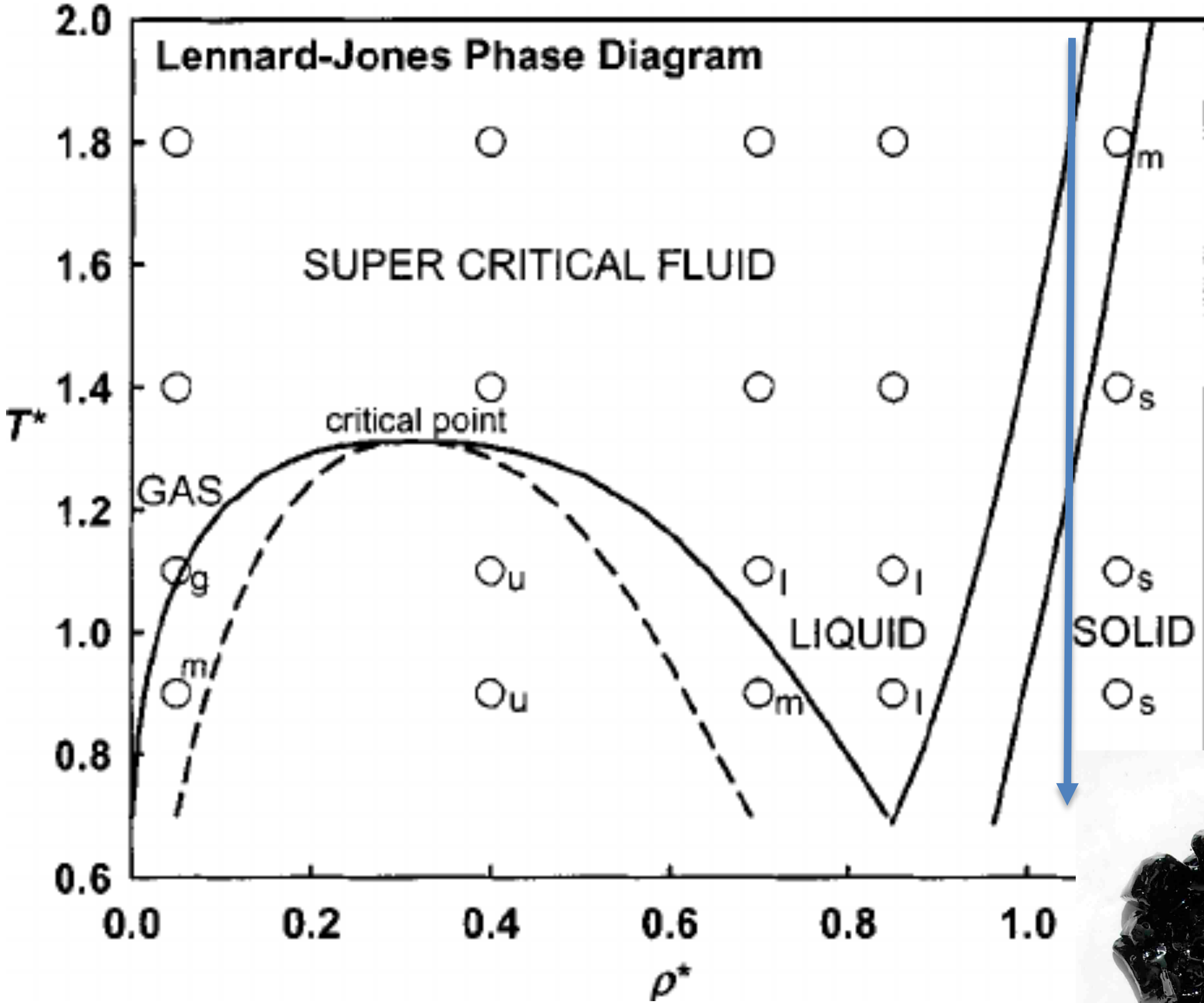
BUT….!

Sometimes things go wrong!

Sometimes ….


Lennard-Jones Phase Diagram
SUPER CRITICAL FLUID
critical point
GAS
LIQUID
SOLID
T*
ρ*
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.0
0.2
0.4
0.6
0.8
1.0

Sometimes ….



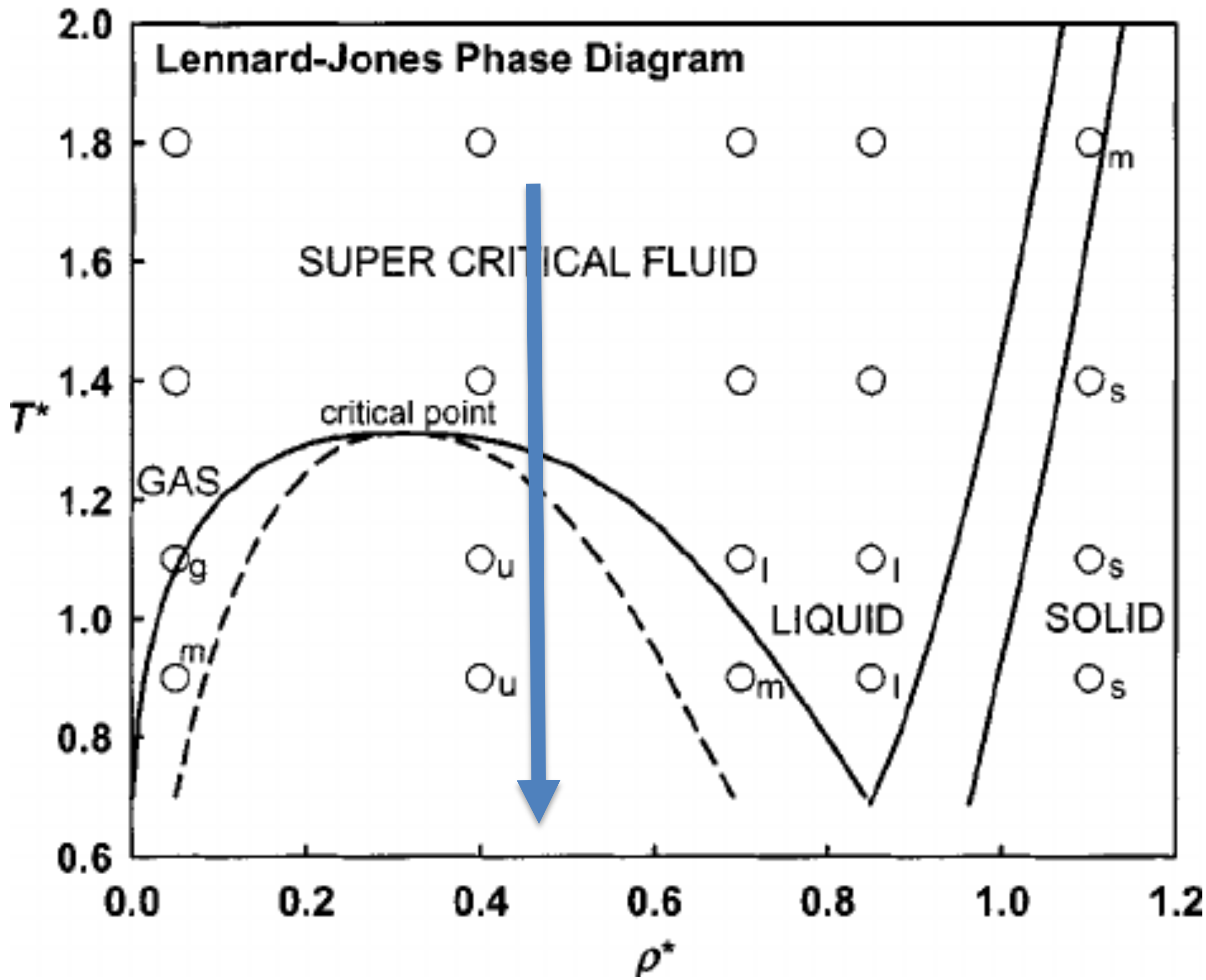
Lennard-Jones Phase Diagram
SUPER CRITICAL FLUID
critical point
GAS
LIQUID
SOLID
g
u
l
m
s
T*
ρ*
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.0
0.2
0.4
0.6
0.8
1.0

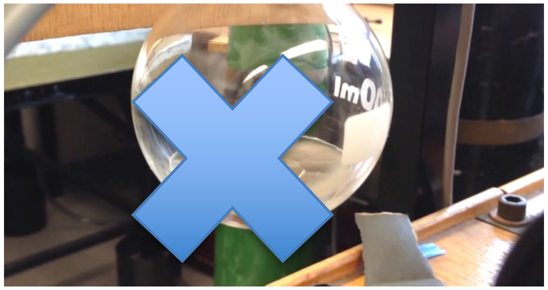
Amorphous Solidification:

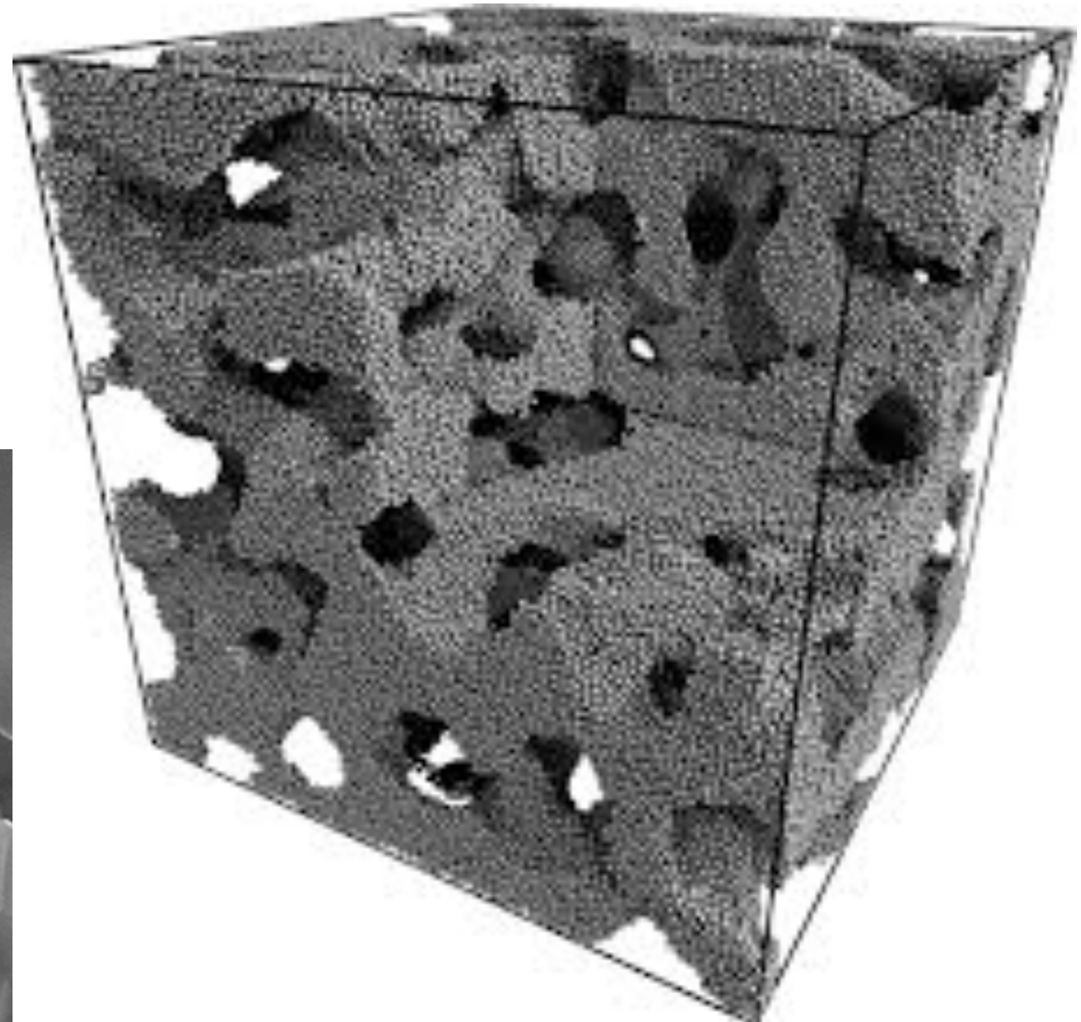
t_w

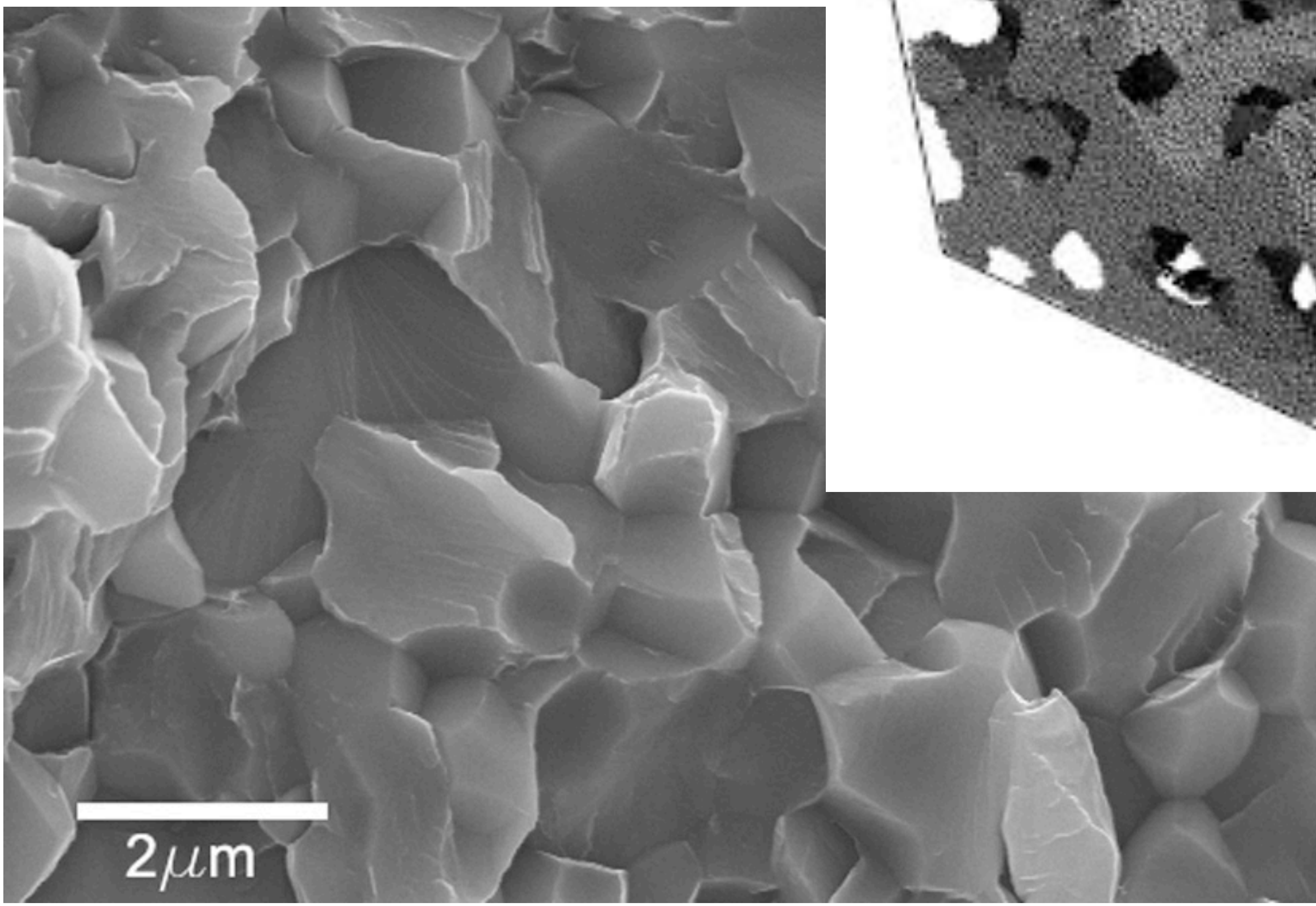
$1/T$

Or, instead of gas-liquid, ...








2μm

NON-EQUILIBRIUM AMORPHOUS SOLIDS

I. Are not stationary (Aging)

Fortschr. Hochpolym.-Forsch., Bd. 3, S. 394—507 (1963)

Transition vitreuse dans les polymères amorphes. Etude phénoménologique

Par

A. J. Kovacs

Centre de Recherches sur les Macromolécules, Strasbourg, France

Avec 25 Figures

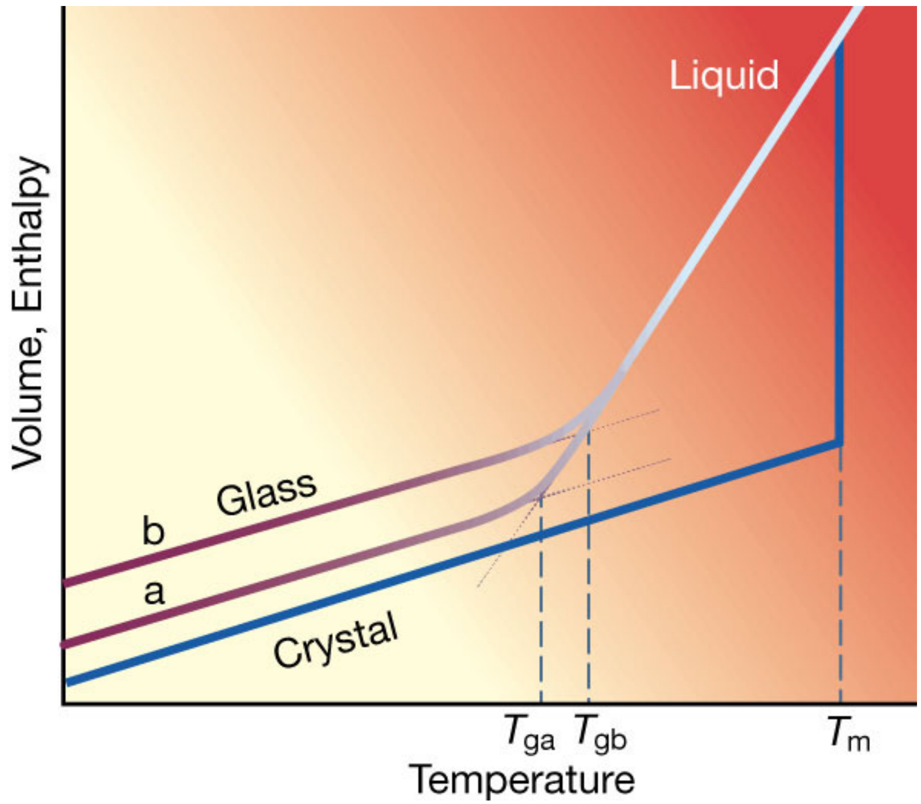
Physical Aging in Plastics and Other Glassy Materials

L. C. E. STRUIK

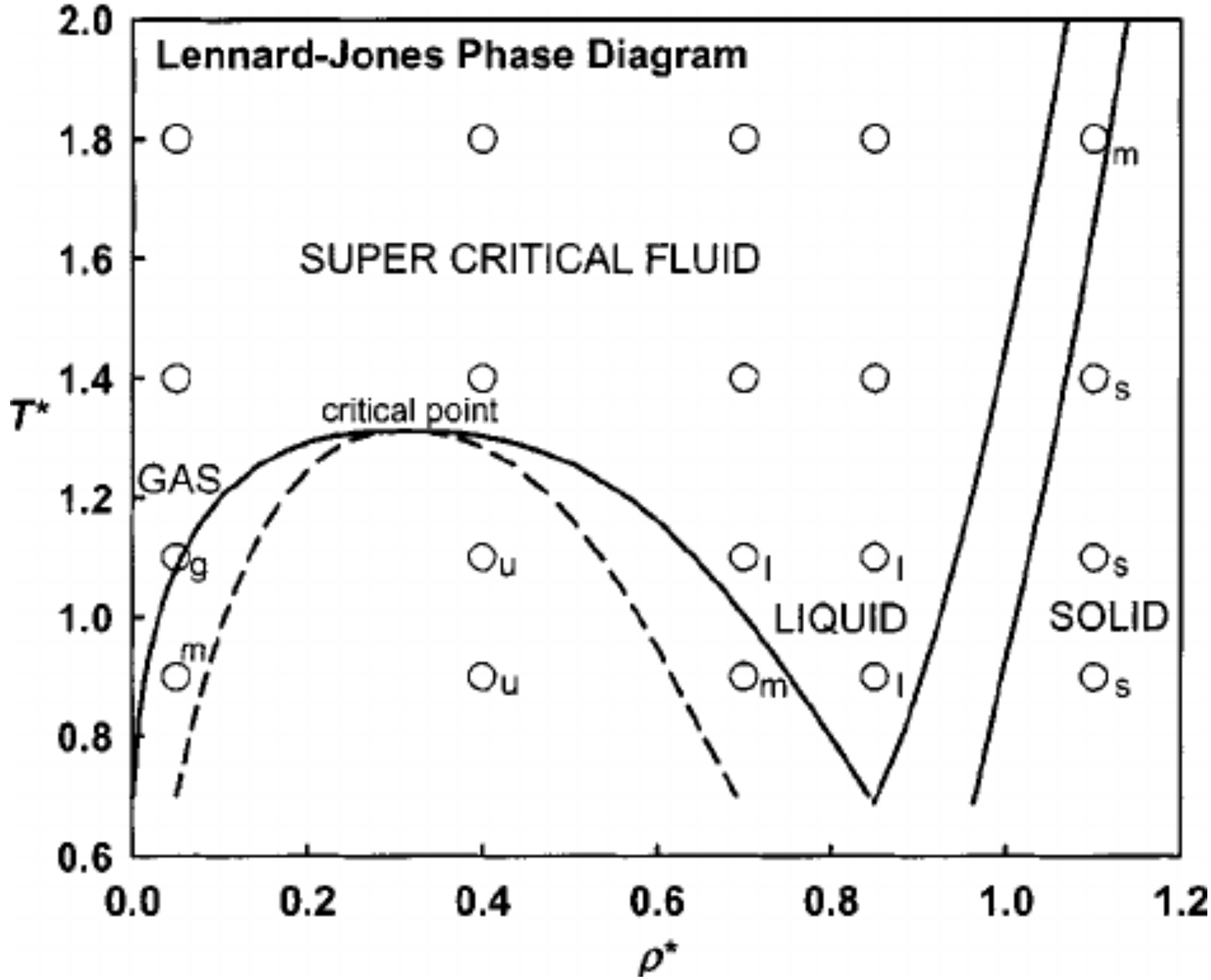
Centraal Laboratorium TNO
Delft, The Netherlands

NON-EQUILIBRIUM AMORPHOUS SOLIDS

II. Depend on preparation protocol.

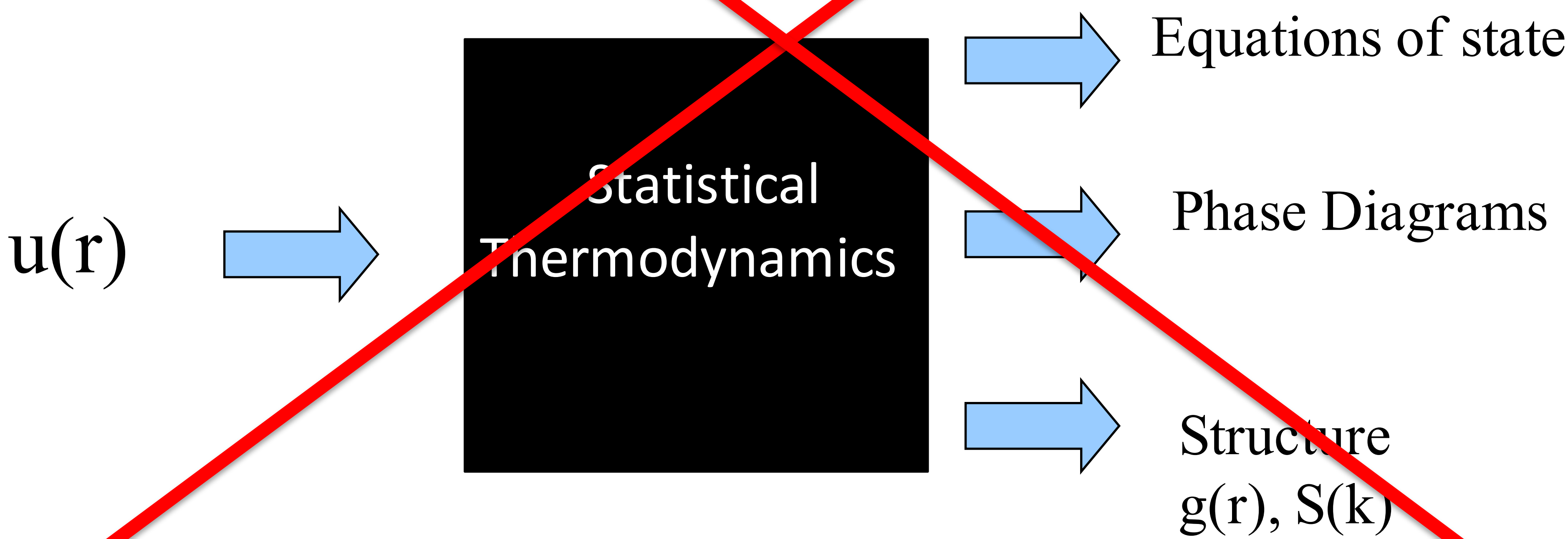


Incompetence or Fundamental Limitation?



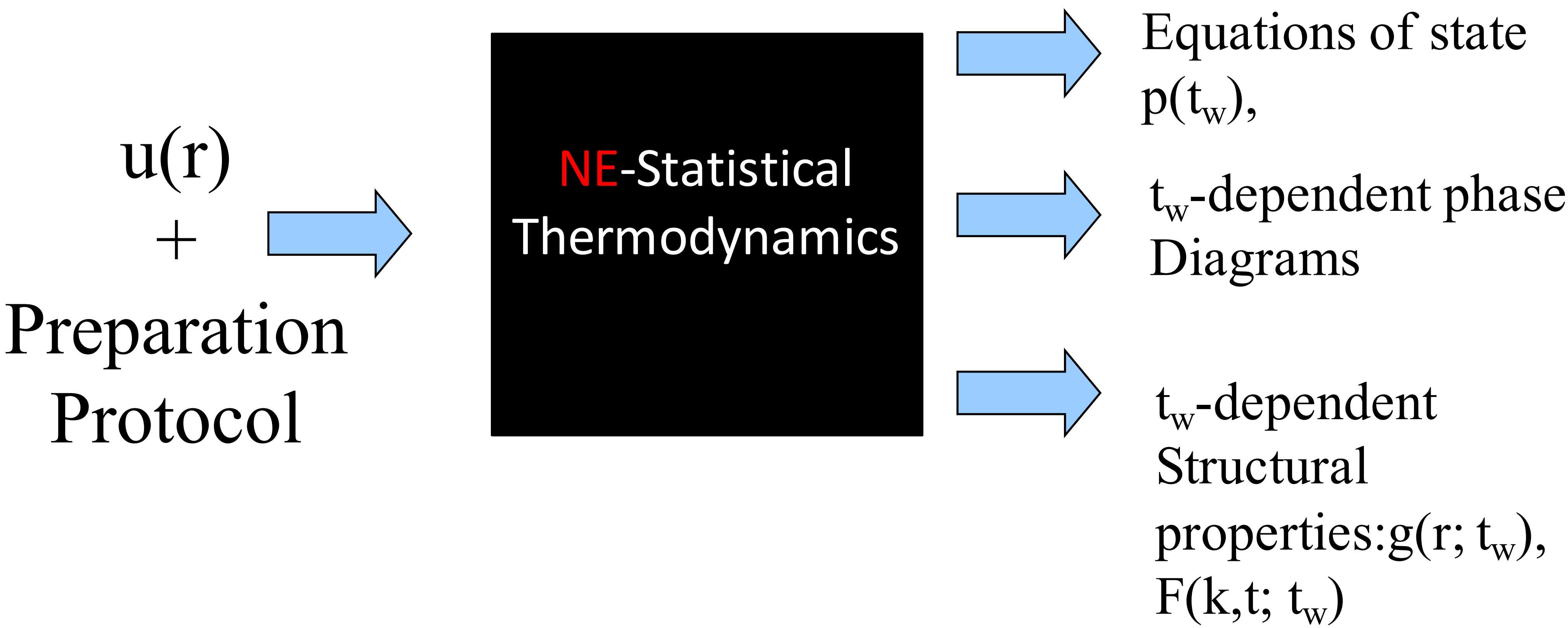
Statistical Thermodynamics

(principle of maximum entropy)

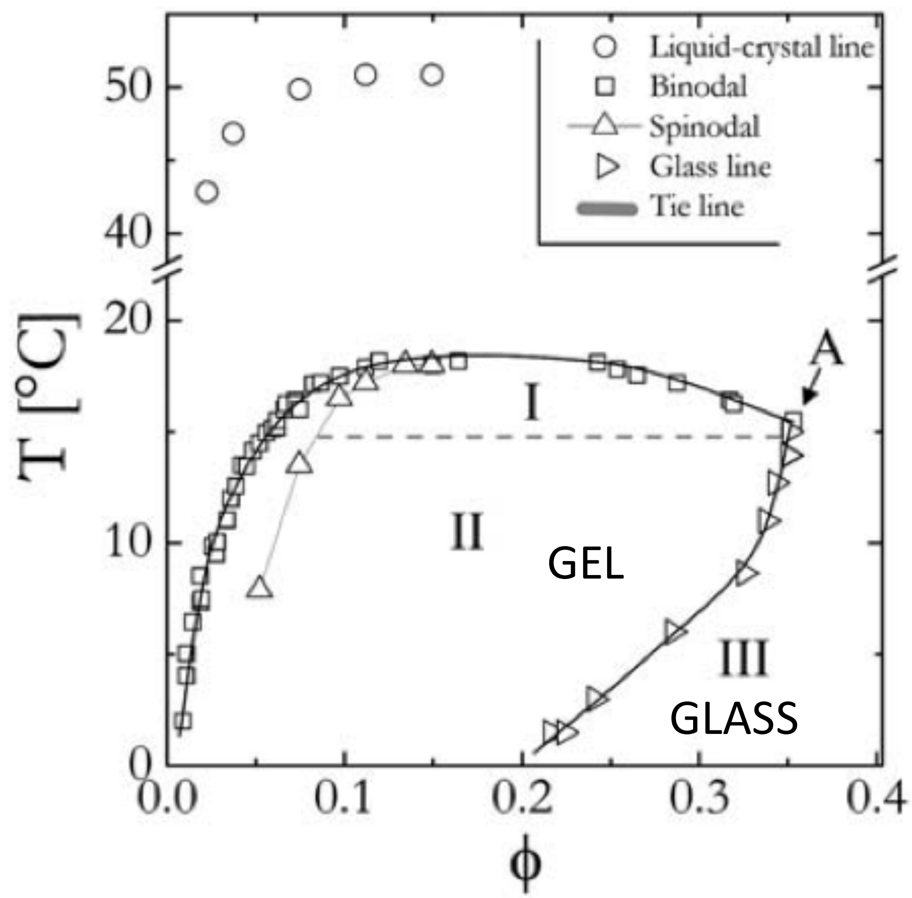


Non-equilibrium Statistical Thermodynamics?

(the principle of maximum entropy?)



SUCH THAT IT *PREDICTS* ***NON-EQUILIBRIUM*** PHASE DIAGRAMS:



Cite this: *Soft Matter*, 2011, **7**, 857

www.softmatter.org

COMMUNICATION

Phase separation and dynamical arrest for particles interacting with mixed potentials—the case of globular proteins revisited†

Thomas Gibaud,‡[a] Frédéric Cardinaux,[a] Johan Bergenholtz,[b] Anna Stradner[c] and Peter Schurtenberger*[d]

CONTENT

- Introduction and advanced summary.
- Fundamental principles: (molecular) thermodynamics.
- Fundamental principles: (molecular) Irreversible thermodynamics.
- *Equilibrium* Self-consistent generalized Langevin equation (SCGLE) theory.
- Aging and irreversibility: the NE-SCGLE theory.
- Full exercise: Lennard-Jones—like liquid.
- Perspectives.

CONTENT

- Introduction and advanced summary.
- Fundamental principles: (molecular) thermodynamics.
- Fundamental principles: (molecular) Irreversible thermodynamics.
- *Equilibrium* Self-consistent generalized Langevin equation (SCGLE) theory.
- Aging and irreversibility: the NE-SCGLE theory.
- Full exercise: Lennard-Jones—like liquid.
- Perspectives.

EQUILIBRIUM SCGLE THEORY

Equilibrium Structure S(k)

$$\hat{F}(k,z;t) = \frac{S(k;t)}{z + \frac{k^2 D^0 S^{-1}(k;t)}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

$$\hat{F}_S(k,z;t) = \frac{1}{z + \frac{k^2 D^0}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

$$\Delta\zeta^*(\tau;t) = \frac{D_0}{3\,(2\pi)^3\,\overline{n}^{(f)}} \int d\mathbf{k}\ k^2 \left[\frac{S(k;t)-1}{S(k;t)}\right]^2 F(k,\tau;t) F_S(k,\tau;t).$$

Equilibrium Dynamic Properties

MODE COUPLING THEORY

Equilibrium Structure S(k)

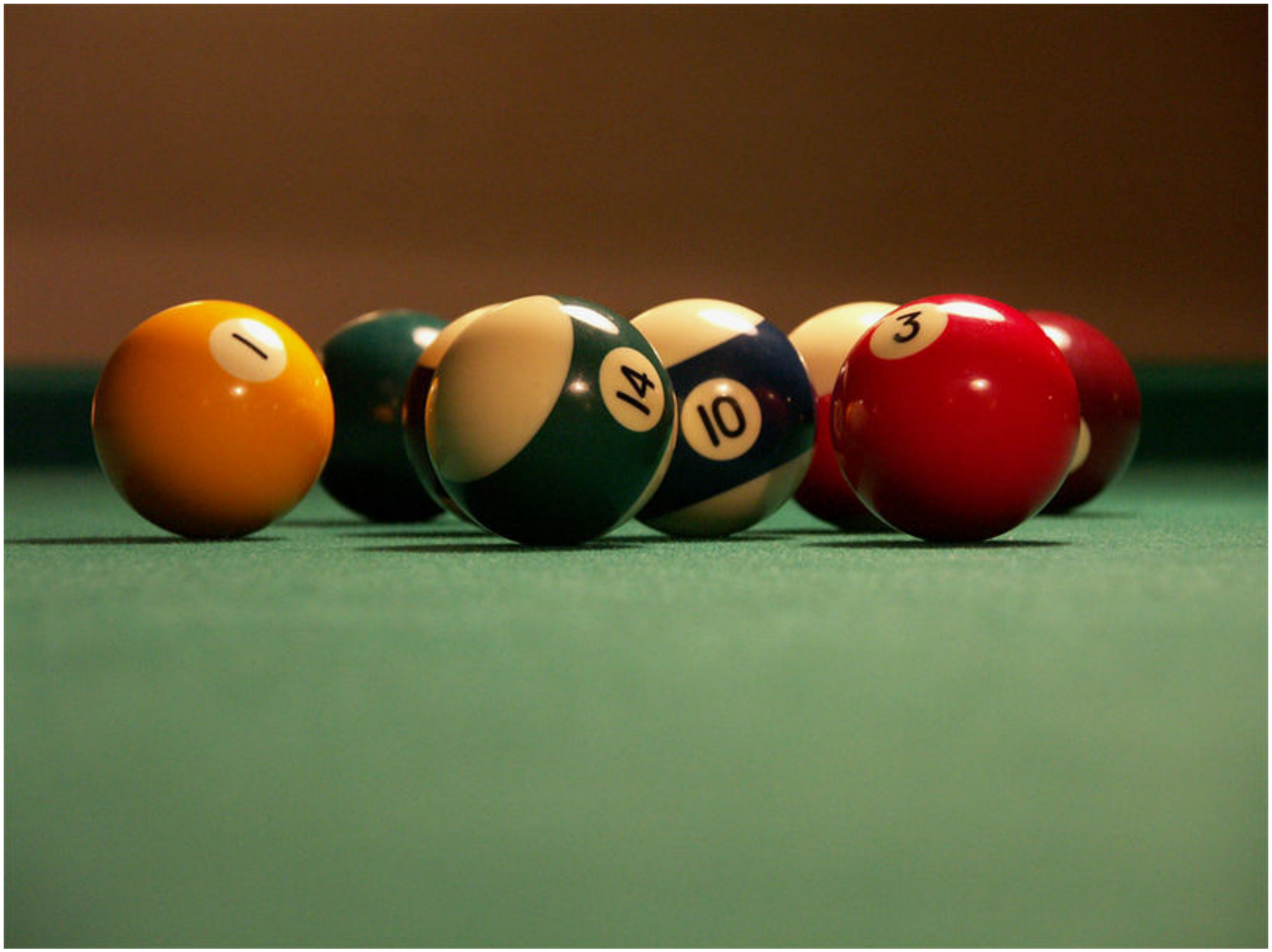
$$\hat{F}(k,z;t) = \frac{S(k;t)}{z + \frac{k^2 D^0 S^{-1}(k;t)}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

$$\hat{F}_S(k,z;t) = \frac{1}{z + \frac{k^2 D^0}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

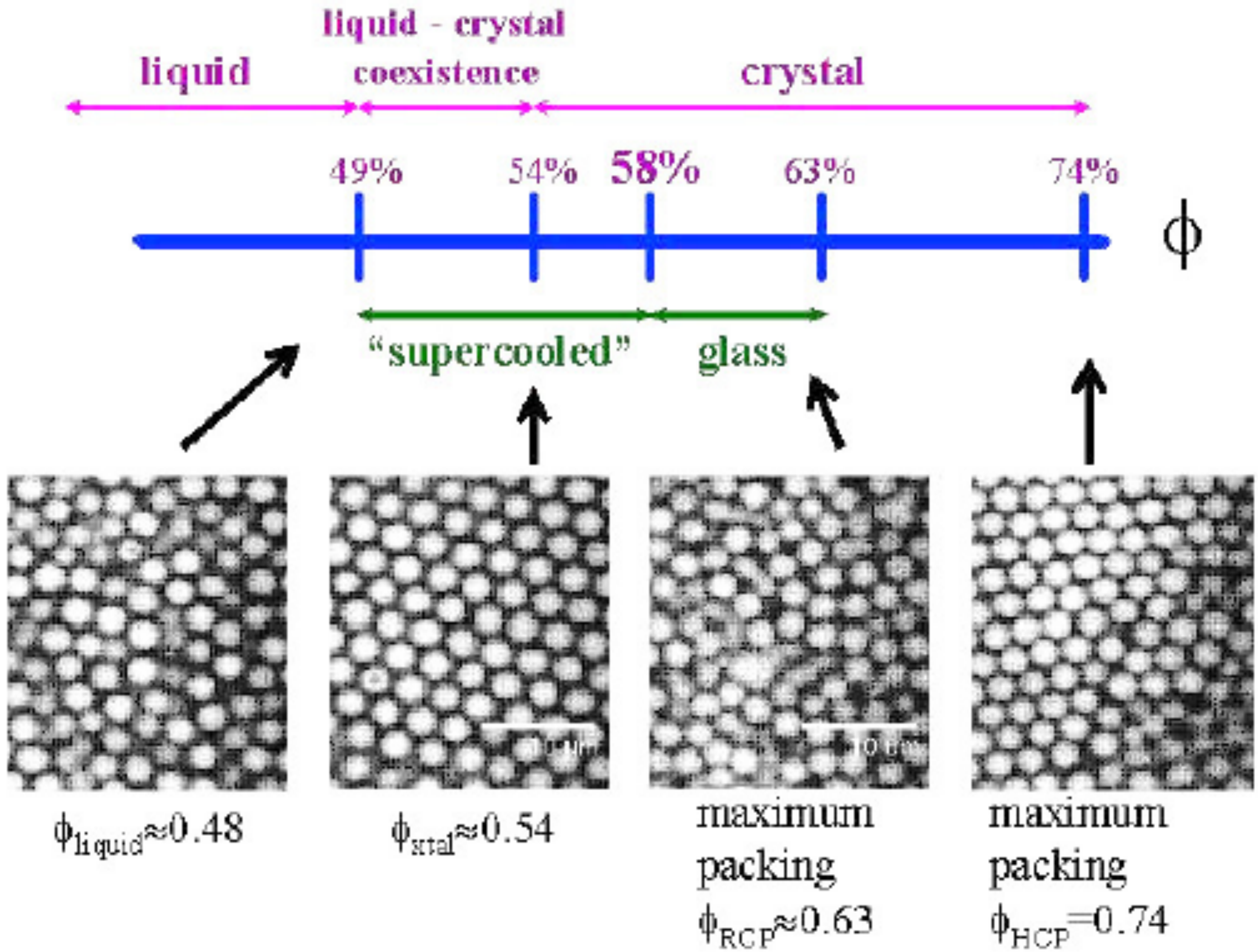
$$\Delta\zeta^*(\tau;t) = \frac{D_0}{3\,(2\pi)^3\,\overline{n}^{(f)}} \int d\mathbf{k}\; k^2 \left[\frac{S(k;t)-1}{S(k;t)}\right]^2 F(k,\tau;t)F_S(k,\tau;t).$$

Equilibrium Dynamic Properties

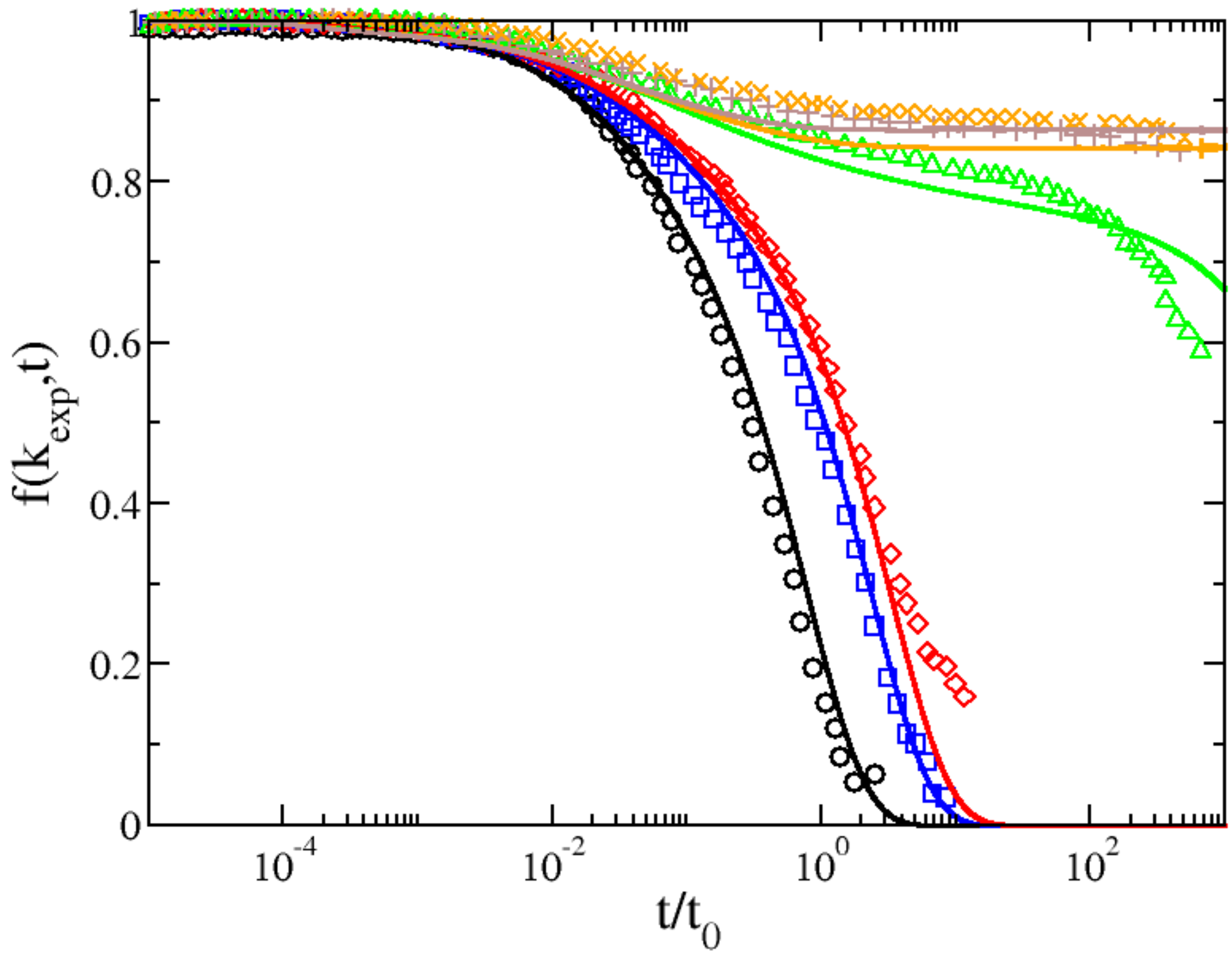
Hard Sphere System



Coloid Glasses

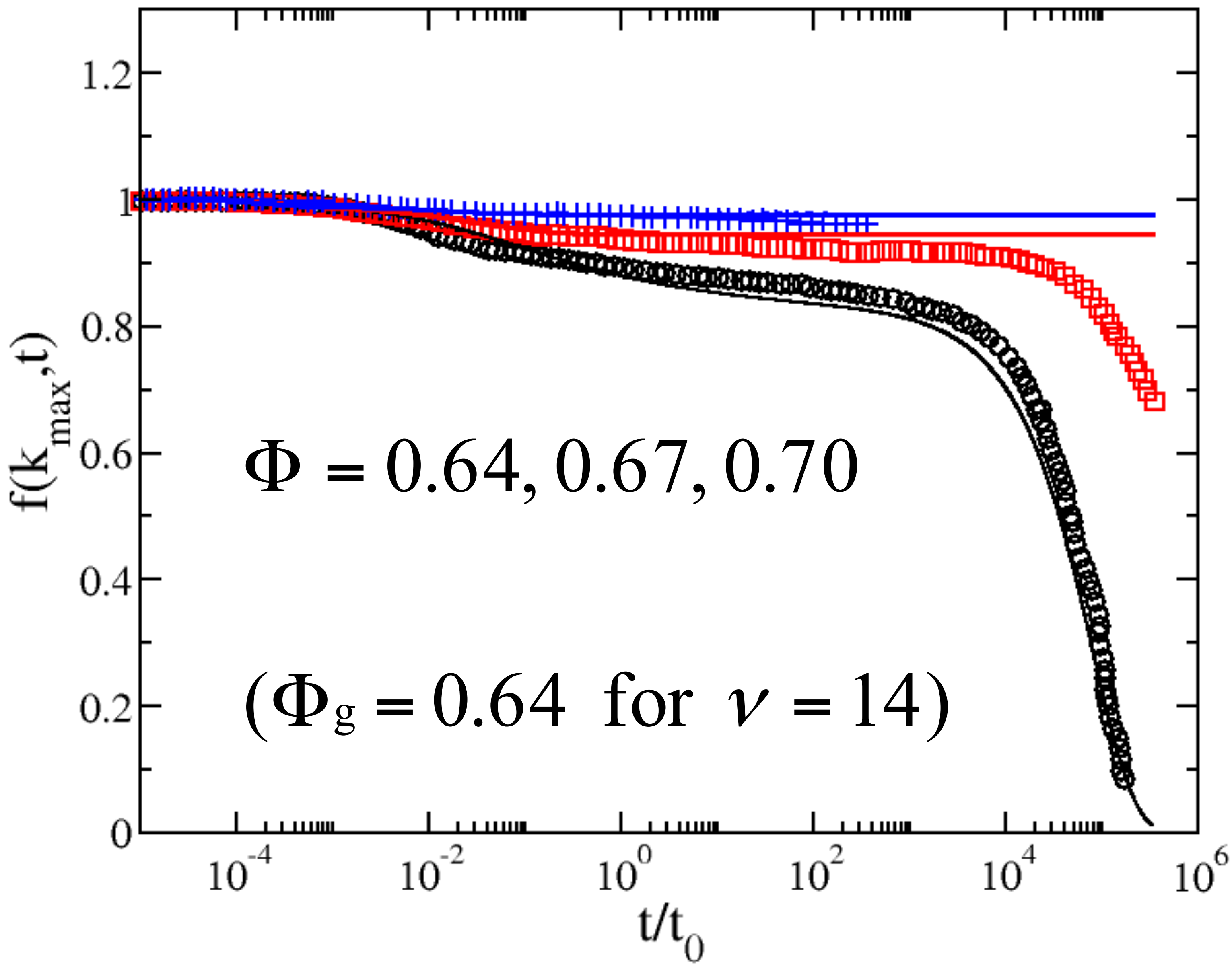


Comparison with Experiment: Hard-Sphere System at the Transition



(P. Ramírez-González et al., PRE **76**: 041504 (2007); JPCM, **21**: 75101 (2008))

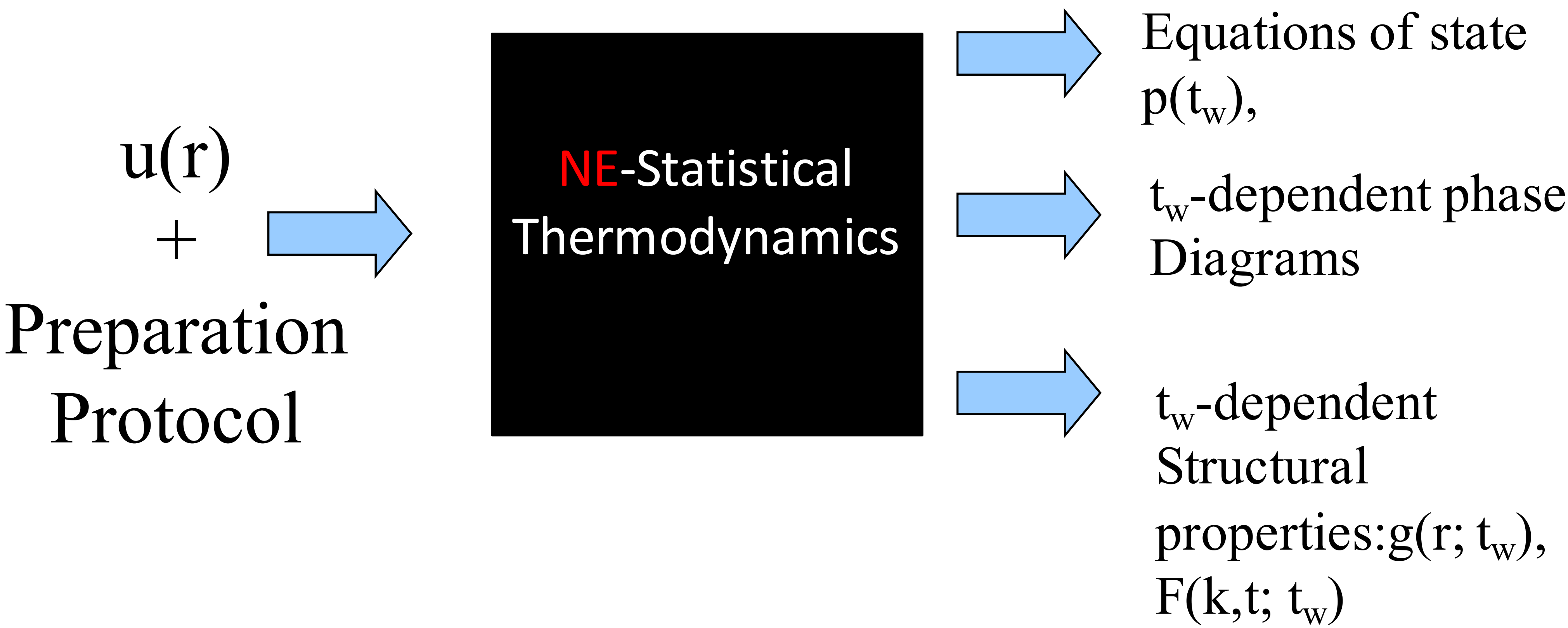
Soft-sphere system (ν=14)



(P. Ramírez-González and M. M.-N., JPCM, **21**: 75101 (2008))

Non-equilibrium Statistical Thermodynamics?

(the principle of maximum entropy?)



Non-equilibrium Statistical Thermodynamics?

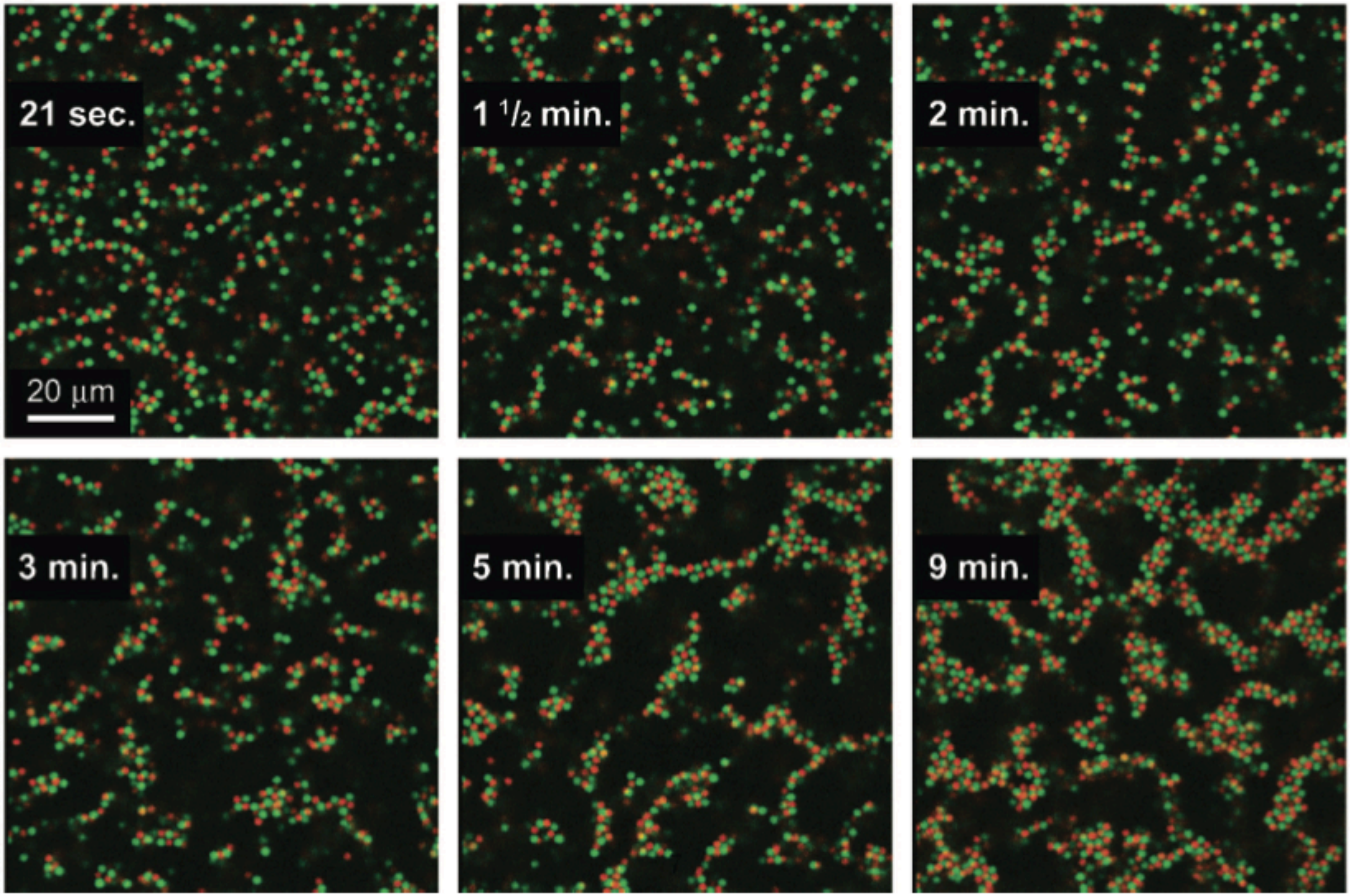
(the principle of maximum entropy?)

How it started?

Gel Formation in Suspensions of Oppositely Charged Colloids: Mechanism and Relation to the Equilibrium Phase Diagram

Eduardo Sanz, Mirjam E. Leunissen, Andrea Fortini, Alfons van Blaaderen, and Marjolein Dijkstra

J. Phys. Chem. B, **2008**, 112 (35), 10861-10872 • DOI: 10.1021/jp801440v • Publication Date (Web): 08 August 2008

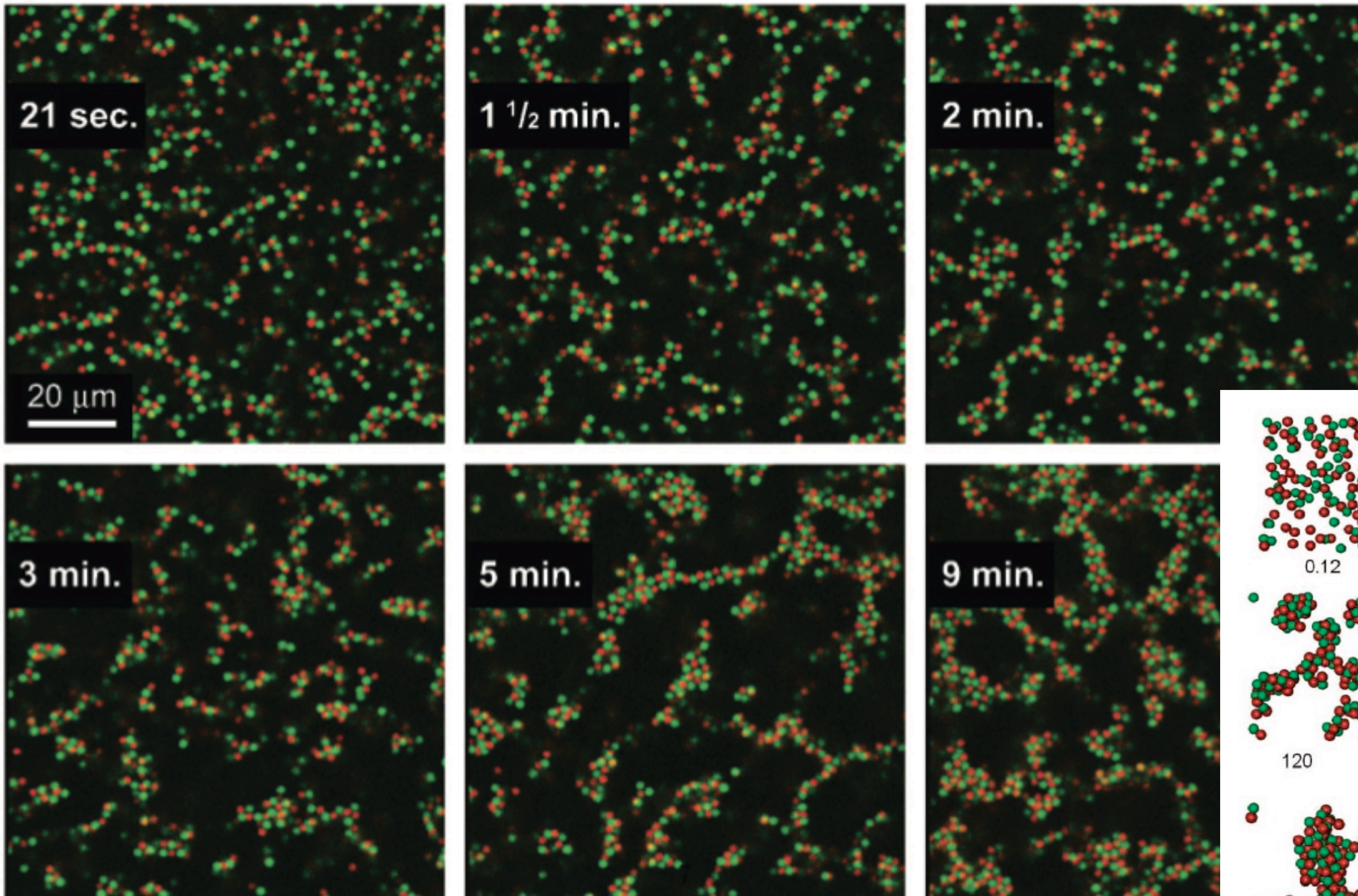


Gel Formation in Suspensions of Oppositely Charged Colloids: Mechanism and Relation to the Equilibrium Phase Diagram

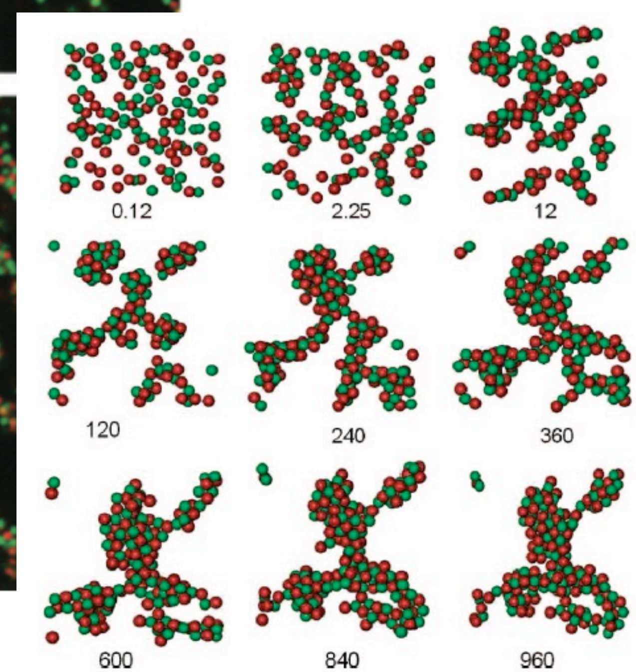
Eduardo Sanz, Mirjam E. Leunissen, Andrea Fortini, Alfons van Blaaderen, and Marjolein Dijkstra

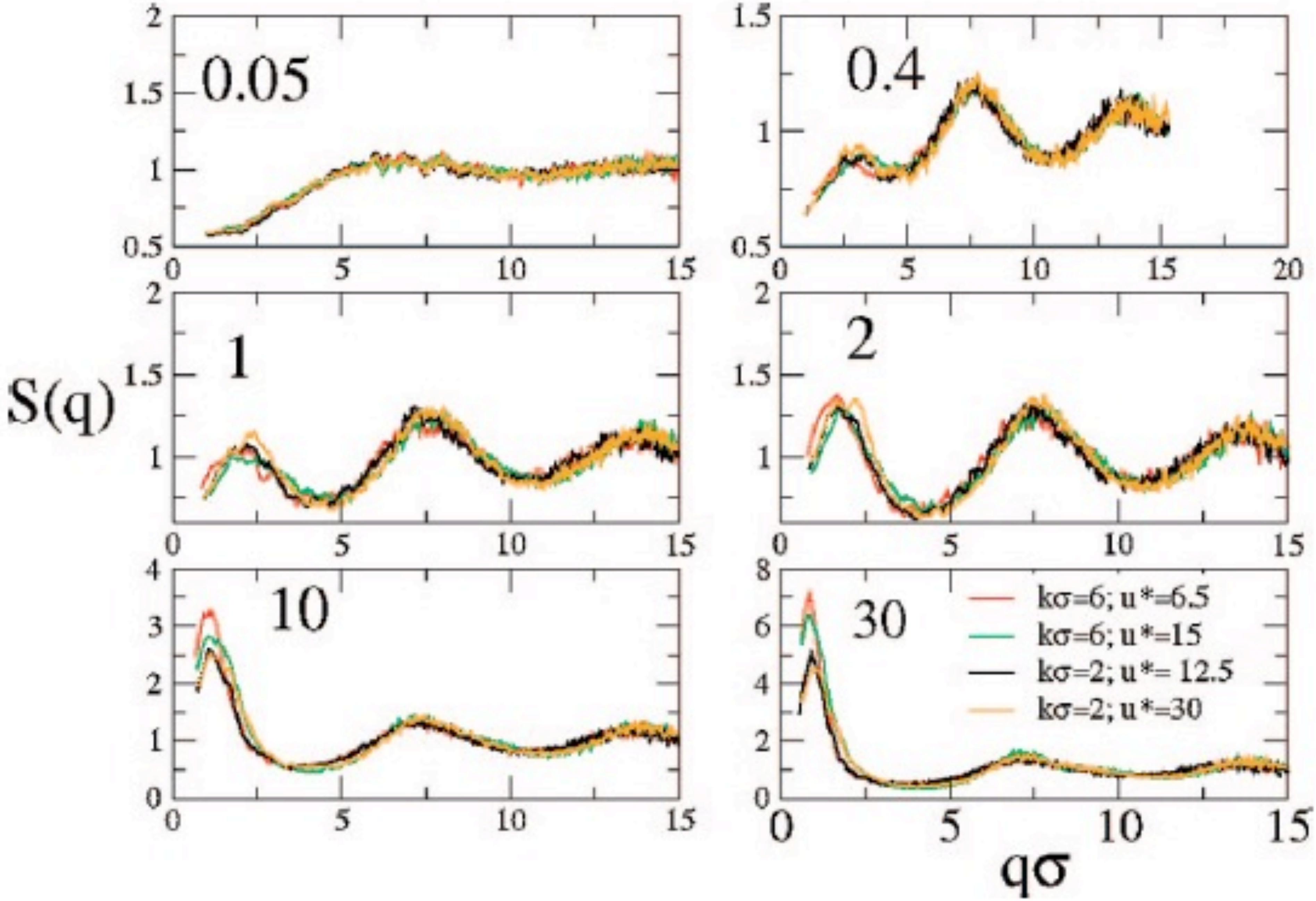
J. Phys. Chem. B, **2008**, 112 (35), 10861-10872 • DOI: 10.1021/jp801440v • Publication Date (Web): 08 August 2008

Experiments:



Simulations:





0.05
0.4
1
2
10
30
S(q)
qσ
kσ=6; u*=6.5
kσ=6; u*=15
kσ=2; u*= 12.5
kσ=2; u*=30

$$\boxed{\frac{\partial S(k;t_w)}{\partial t_w} = ?}$$

THE NON-EQUILIBRIUM SELF-CONSISTENT GENERALIZED LANGEVIN EQUATION (NE-SCGLE) THEORY:

PHYSICAL REVIEW E **82**, 061503 (2010)

General nonequilibrium theory of colloid dynamics

Pedro Ramírez-González and Magdaleno Medina-Noyola
Instituto de Física "Manuel Sandoval Vallarta," Universidad Autónoma de San Luis Potosí, Álvaro Obregón 64, San Luis Potosí, 78000 San Luis Potosí, Mexico

(Received 18 December 2009; revised manuscript received 27 October 2010; published 14 December 2010)

NE-SCGLE THEORY OF IRREVERSIBLE PROCESSES

- **General Theory of Nonequilibrium Relaxation:** P. Ramírez-González and M. Medina-Noyola Phys. Rev. E **82, 061503 (2010);** Ibid. **Phys. Rev. E 82 061504 (2010)**
- **Equilibration and aging of dense soft-sphere glass-forming liquids** L. E. Sánchez-Díaz, P. Ramírez-González and M. Medina-Noyola **Phys. Rev. E 87, 052306 (2013)**
- **Non-equilibrium dynamics of glass-forming liquid mixtures** L. E. Sánchez-Díaz, E. Lázaro-Lázaro, J.M. Olais-Govea, and M. Medina-Noyola, **J. Chem. Phys. 140, 234501 (2014)**
- **Non-equilibrium Theory of Arrested Spinodal Decomposition** J. M. Olais-Govea, L. López-Flores and M. Medina-Noyola, **J. Chem. Phys. 143, 174505 (2015).**
- **Equilibration and Aging of Liquids of Non-Spherically Interacting Particles**, E.C. Cortés-Morales, L.F. Elizondo-Aguilera, and M. Medina-Noyola, **J. Phys. Chem. B, 120 7975 (2016).**
- **Crossover from Equilibration to Aging: (Non-equilibrium) Theory vs. Simulations,** P. Mendoza-Méndez, E. Lázaro-Lázaro, L. E. Sánchez-Díaz, P. E. Ramírez-González, G. Pérez-Ángel, and M. Medina-Noyola. **Phys. Rev. E 96, 022608 (2017).**
- **Nonequilibrium kinetics of the transformation of liquids into physical gels,** J. M. Olais-Govea, L. López-Flores and M. Medina-Noyola, **Phys. Rev. E Rapid Commun. (in press, 2018).**

CONTENT

- Introduction and advanced summary.
- Fundamental principles: (molecular) thermodynamics.
- Fundamental principles: (molecular) Irreversible thermodynamics.
- *Equilibrium* Self-consistent generalized Langevin equation (SCGLE) theory.
- Aging and irreversibility: the NE-SCGLE theory.
- Full exercise: Lennard-Jones—like liquid.
- Perspectives.

Classical Thermodynamics
(Callen)

FIRST LAW: **A**=[A_1 , A_2 ,…, A_M].
(And the energy is one of them.)

SECOND LAW:
Fundamental Thermodynamic Relation:

$$S = S[\mathbf{A}]$$

Thermodynamic Theory of Fluctuations (Components of A, random variables)

$$P[\mathbf{A}] = (const.) exp\left[\left(S[\mathbf{A}] - S[\mathbf{A}^{eq}]\right)/k_B\right]$$

$$\overline{(\delta\mathbf{A})(\delta\mathbf{A})^T} \circ \mathcal{E}^{eq} = \mathbf{I}$$

$$\mathcal{E}^{eq}_{ij} \equiv -\frac{1}{k_B}\left(\frac{\partial^2 S[\mathbf{A}]}{\partial A_i \partial A_j}\right)_{\mathbf{A}=\mathbf{A}^{eq}}$$

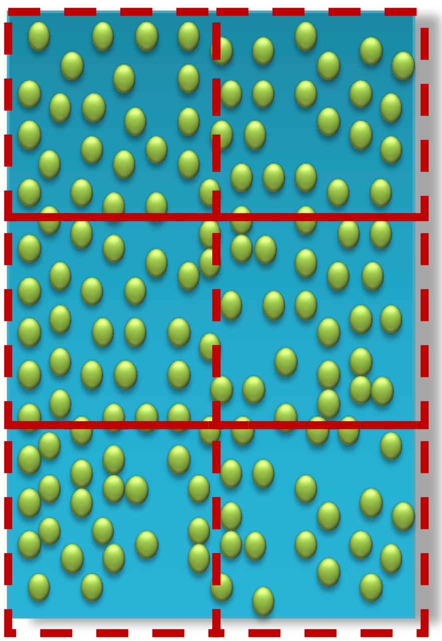
Thermodynamic Theory of Fluctuations (Components of A, random variables)

EQUILIBRIUM CONDITION FOR THE SECOND MOMENTS

$$\overline{(\delta \mathbf{A})(\delta \mathbf{A})^T} \circ \mathcal{E}^{eq} = \mathbf{I}$$

$$\mathcal{E}_{ij}^{eq} \equiv -\frac{1}{k_B}\left(\frac{\partial^2 S[\mathbf{A}]}{\partial A_i \partial A_j}\right)_{\mathbf{A}=\mathbf{A}^{eq}}$$

Example: A simple liquid

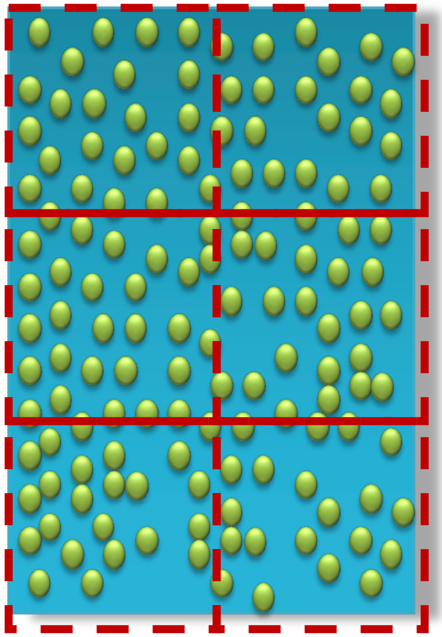


$$E^{(r)}, N^{(r)} \text{ and } \cancel{V}^{(r)}$$

$$r = 1, 2, ..., C.$$

$$\boxed{S = S[\mathbf{E}, \mathbf{N}, \cancel{\mathbf{V}}]}$$

Example: A simple liquid



$$E^{(r)}, N^{(r)} \text{ and } V^{(r)}$$

$$r = 1, 2, ..., C.$$

$$\beta\mu^{(r)}[\beta; \mathbf{N}] = \beta\mu^{o}(\beta) + \ln(N^{(r)}/\Delta V) - c^{(r)}[\beta; \mathbf{N}] + \beta\psi^{(r)}$$

Example: A simple liquid

$$\sum_{r'=1}^{C} < \delta N^{(r)} \delta N^{(r')} > E^{(r',r'')} = \delta_{r,r''}$$

$$E^{(r',r'')} \equiv \left(\frac{\partial \beta \mu^{(r')}[\beta, \mathbf{N}]}{\partial N^{(r'')}} \right)_{\mathbf{N}=\mathbf{N}_{eq}}$$

Example: A simple liquid

$$S^{(eq)}(k;\phi,T) = 1/\overline{n}\mathcal{E}_h(k;\phi,T)$$

$$E^{(r',r'')} \equiv \left(\frac{\partial\beta\mu^{(r')}[\beta,\mathbf{N}]}{\partial N^{(r'')}}\right)_{\mathbf{N}=\mathbf{N}_{eq}}$$

Example: A simple liquid

$$S^{(eq)}(k;\phi,T) = 1/\overline{n}\mathcal{E}_h(k;\phi,T)$$

(Equilibrium condition for the static structure factor)

BIBLIOGRAPHY

- https://www.dropbox.com/sh/dnub6awebf715rt/AAAhmk6-u611s7l1J-09lxFDa?dl=0

- medina@ifisica.uaslp.mx

CONTENT

- Introduction and advanced summary.
- Fundamental principles: (molecular) thermodynamics.
- Fundamental principles: (molecular) Irreversible thermodynamics.
- *Equilibrium* Self-consistent generalized Langevin equation (SCGLE) theory.
- Aging and irreversibility: the NE-SCGLE theory.
- Full exercise: Lennard-Jones—like liquid.
- Perspectives.

Non-equilibrium Statistical Thermodynamics?

(the principle of maximum entropy?)

Kinetic theory

Non-equilibrium Statistical Thermodynamics?

(the principle of maximum entropy?)

Brownian Motion

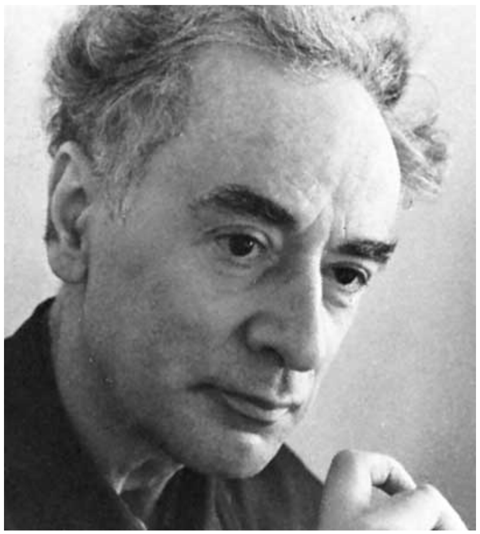
Non-equilibrium Statistical Thermodynamics?

(the principle of maximum entropy?)

Irreversible thermodynamics

Non-equilibrium Statistical Thermodynamics?

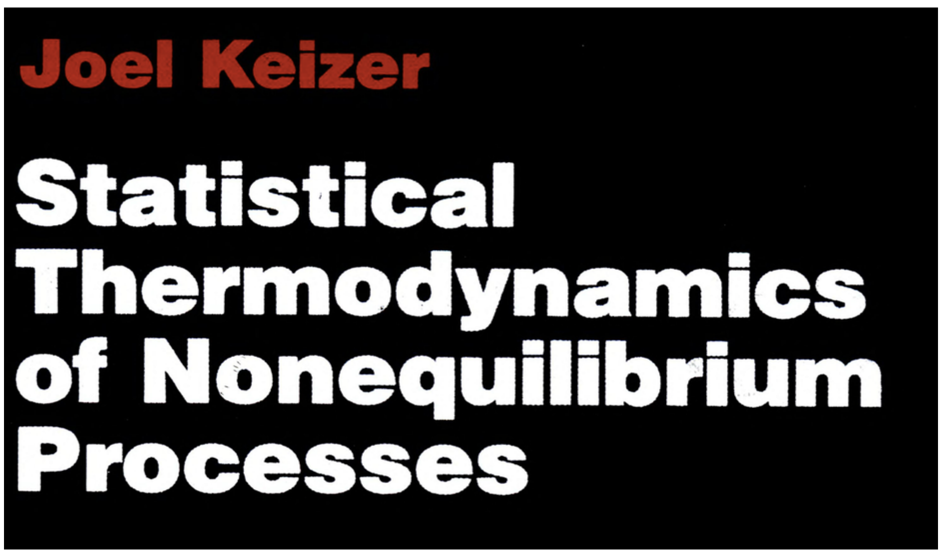
(the principle of maximum entropy?)



Fluctuating hydrodynamics

Non-equilibrium Statistical Thermodynamics?

(the principle of maximum entropy?)



Springer-Verlag
New York Berlin Heidelberg
London Paris Tokyo

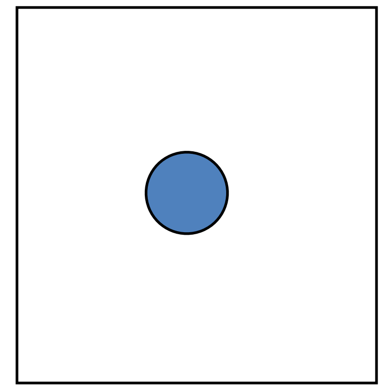
Non-equilibrium Statistical Thermodynamics?

(the principle of maximum entropy?)

Brownian Motion

Langevin Equation:

$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t)$$



$$\left\langle f^0(t) f(0) \right\rangle = \gamma\delta(t)$$

$$\left\langle \mathbf{V}(t)\mathbf{V}(t) \right\rangle_{t\to\infty} = \overleftrightarrow{I}(k_B T / M)$$

Ornstein-Uhlenbeck Process

$$\delta a_i(t) \quad (i = 1,2,\ldots,m)$$

$$\frac{d\delta a(t)}{dt} = -H \cdot \delta a(t) + f(t)$$

With f(t) being a "white" noise: Gaussian, stationary, and δ-correlated ($\langle f(t) f(0) \rangle = \gamma \delta(t)$).

Ornstein-Uhlenbeck Process

$$\delta a_i(t) \quad (i = 1,2,\ldots,m)$$

$$\frac{d\delta a(t)}{dt} = -H \cdot \delta a(t) + f(t)$$

With f(t) being a "white" noise: Gaussian, stationary, and δ-correlated ($\langle f(t) f(0) \rangle = \gamma \delta(t)$).

The Ornstein-Uhlenbeck process δa(t) thus defined is Gaussian, stationary, and Markovian

Important properties of an Ornstein-Uhlenbeck process:

(0): The *fluctuation-dissipation Theorem:*

$$\langle f(t) f(0) \rangle = \gamma \delta(t)$$

$$\boxed{\gamma = H \cdot \sigma^{ss} + \sigma^{ss} \cdot H^{T}}$$

$$\sigma^{ss} = \langle \delta a(t) \delta a(t) \rangle^{ss}$$

Important properties of an Ornstein-Uhlenbeck process:

(I) On the mean value:

$$\frac{d\Delta\overline{\mathbf{a}}(t)}{dt} = -\mathcal{H} \circ \Delta\overline{\mathbf{a}}(t)$$

where $\Delta\overline{\mathbf{a}}(t) \equiv \overline{\mathbf{a}}^0(t) - \mathbf{a}^{ss}$

(II) On the covariance $\sigma(t) \equiv \overline{\delta\mathbf{a}(t)\delta\mathbf{a}^\dagger(t)}$

$$\frac{d\sigma(t)}{dt} = -H \cdot \sigma(t) - \sigma(t) \cdot H^T + \gamma$$

(with $\gamma = H \cdot \sigma^{ss} + \sigma^{ss} \cdot H^T$)

(III) On the structure of the relaxation matrix:

$$\mathcal{H} = \mathcal{L} \circ \sigma^{ss-1}$$

(IV) On the structure of the "linear laws":

$$\frac{d\Delta\overline{\mathbf{a}}(t)}{dt} = -\mathcal{L} \circ \sigma^{ss-1} \circ \Delta\overline{\mathbf{a}}(t)$$

(V) The OU process also comes with a handy exact expression for the second moment $\mathbf{W}(t) \equiv < \Delta\mathbf{x}(t)\Delta\mathbf{x}^{\dagger}(t) >$ of the "displacement" $\Delta\mathbf{x}(t) \equiv \int_0^t \mathbf{a}(\tau)d\tau$. For the mono-component case ($\nu = 1$), such an expression reads

$$W(t) = 2H^{-1}\sigma^{ss}[t + H^{-1}(e^{-Ht} - 1)], \tag{2}$$

which at short times is quadratic in the time t, and at long times is linear, i.e.,

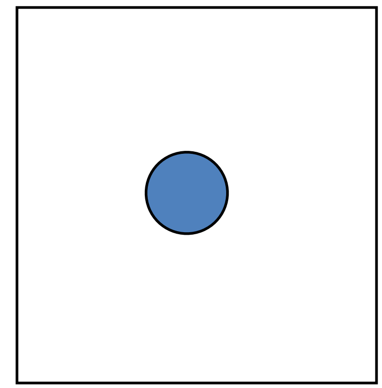
$$W(t) \approx \begin{cases} \sigma^{ss}t^2 & \text{if } t < H^{-1} \\ 2\sigma^{ss}H^{-1}t & \text{if } t > H^{-1}. \end{cases} \tag{3}$$

Introducing the dimensionless variables $t^* \equiv tH$ and $W^* \equiv W(t)H^2/\sigma^{ss}$ one can rewrite Eq.(2) as the following master equation:

$$W^*(t^*) = 2[t^* + e^{-t^*} - 1]. \tag{4}$$

Langevin Equation:

$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t)$$



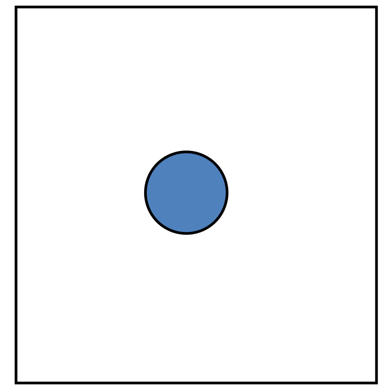
$$\left\langle f^0(t) f(0) \right\rangle = \gamma\delta(t)$$

$$\left\langle \mathbf{V}(t)\mathbf{V}(t) \right\rangle_{t\to\infty} = \overleftrightarrow{I}(k_B T / M)$$

$$\left(\sigma^{ss} = \langle \delta a(t)\delta a(t)\rangle^{ss}\right)$$

Langevin Equation:

$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t)$$



$$\left\langle f^0(t) f(0) \right\rangle = \gamma\delta(t)$$

$$\left\langle \mathbf{V}(t)\mathbf{V}(t) \right\rangle_{t\to\infty} = \ ?$$

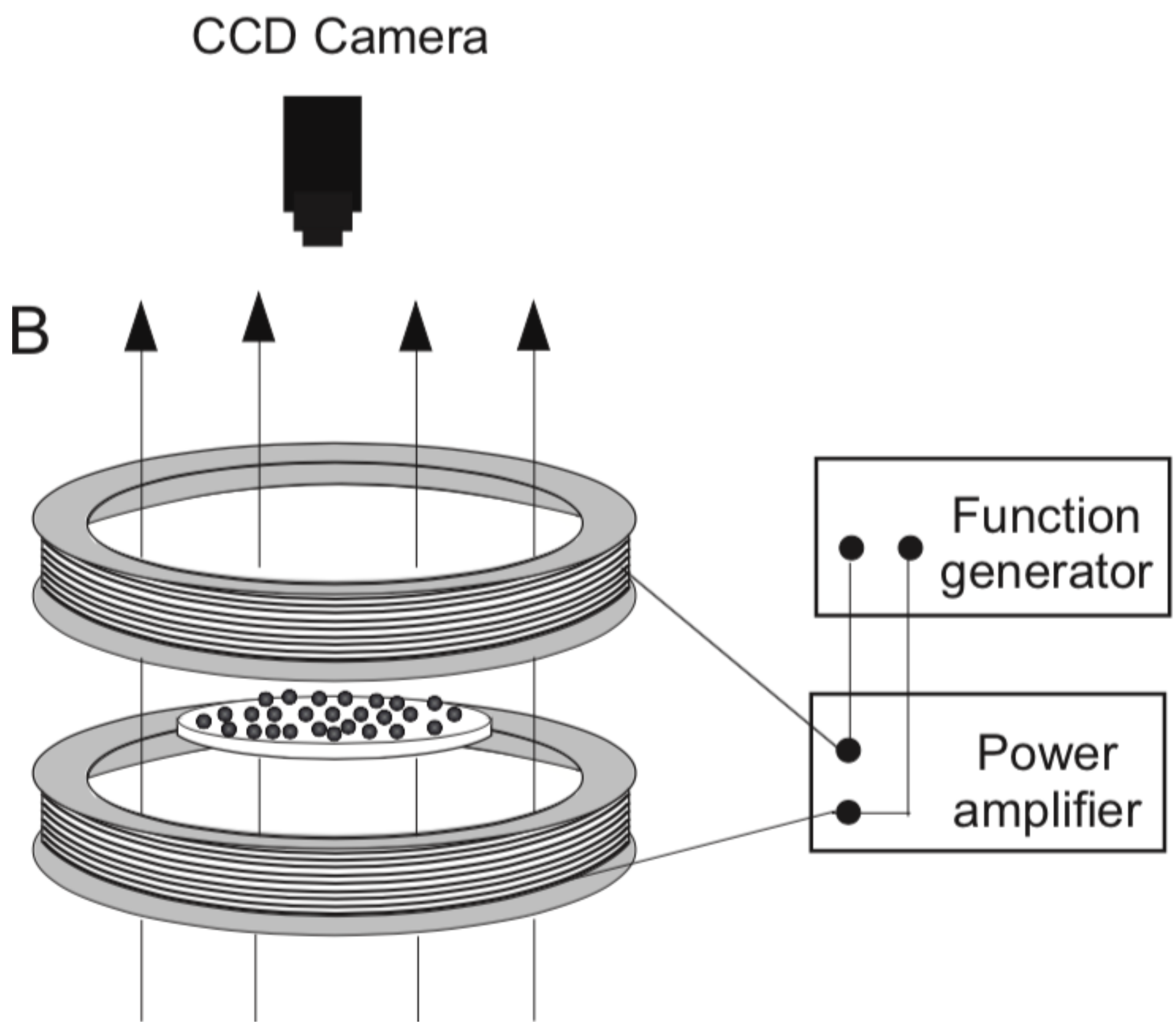
OPEN

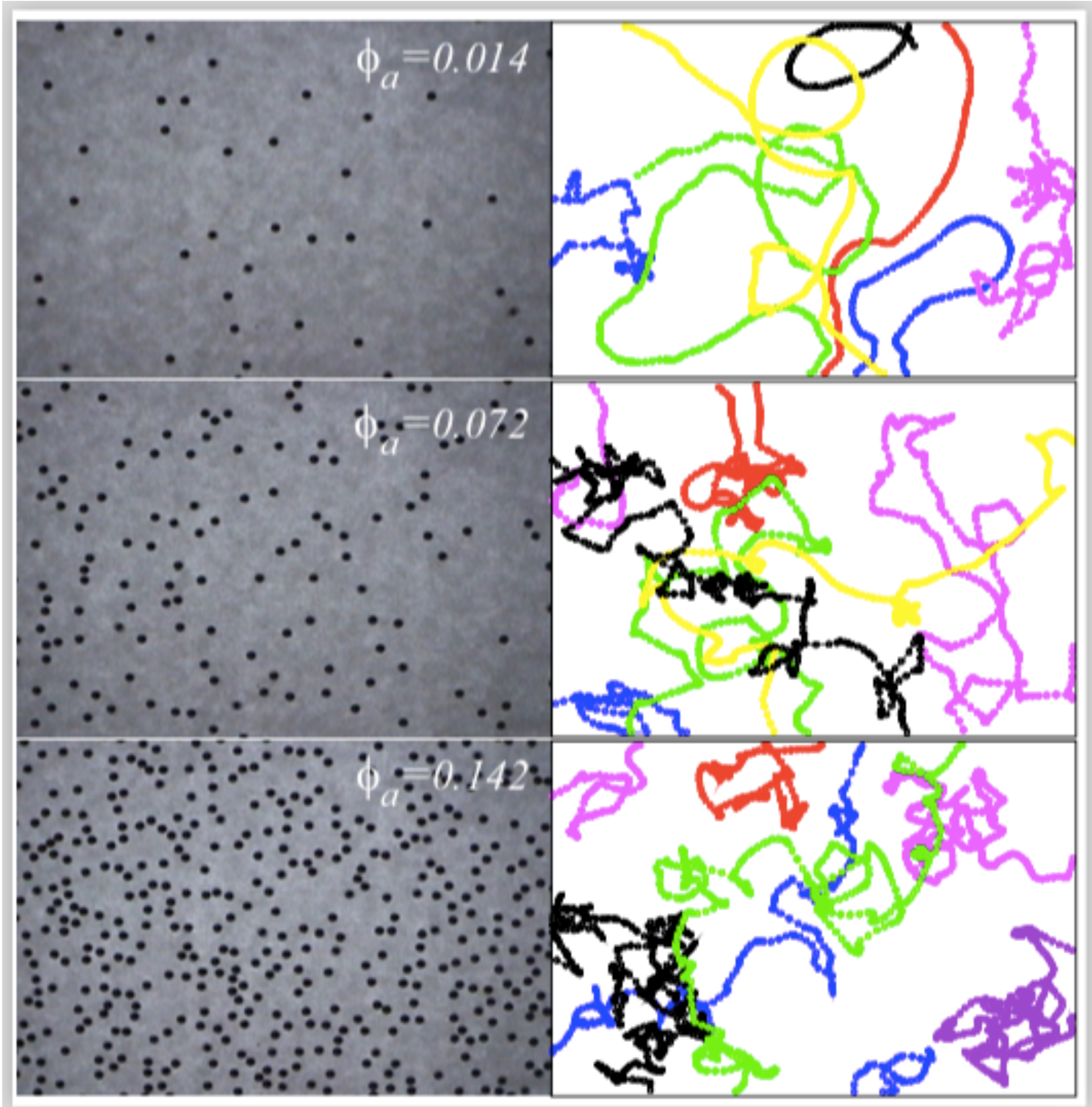
Brownian motion in non-equilibrium systems and the Ornstein-Uhlenbeck stochastic process

Received: 21 July 2017
Accepted: 18 September 2017
Published online: 03 October 2017

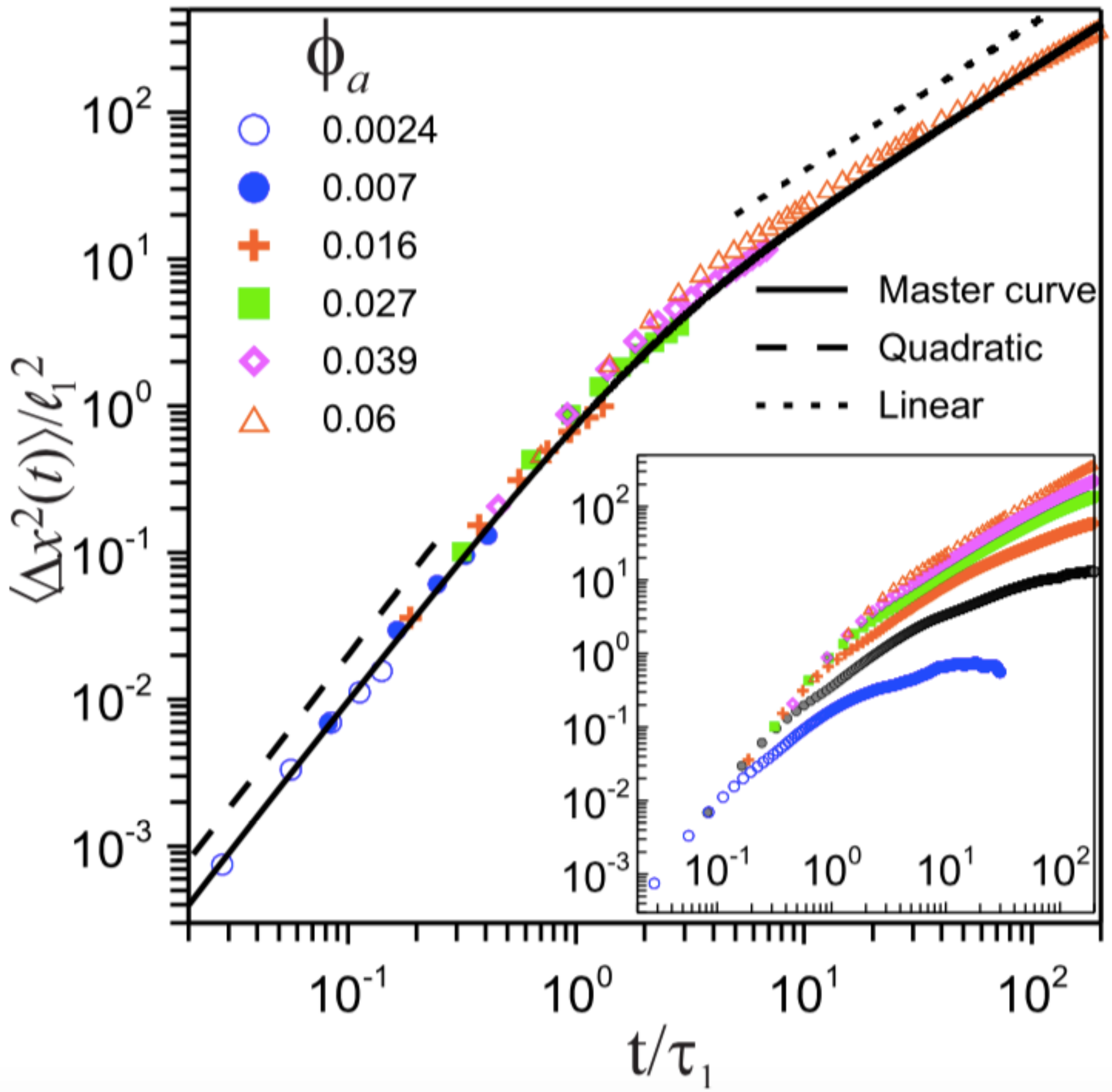
F. Donado[1], R. E. Moctezuma[2], L. López-Flores[3], M. Medina-Noyola[3] & J. L. Arauz-Lara[3]

SCIENTIFIC REPORTS | 7: *12614* | DOI:10.1038/s41598-017-12737-1


CCD Camera
B
Function
generator
Power
amplifier



ϕa=0.014
ϕa=0.072
ϕa=0.142



ϕ_a
0.0024
0.007
0.016
0.027
0.039
0.06
Master curve
Quadratic
Linear
$\langle \Delta x^2(t) \rangle / \ell_1^2$
t/τ_1
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}

Onsager's Theory of Thermal fluctuations

Onsager's Theory:

I. Thermal fluctuations behave as an Ornstein-Uhlenbeck process

II. Thermodynamic equilibrium:

$$\sigma^{ss} = \langle \delta a(t) \delta a(t) \rangle^{ss}$$ **is given by** $$\boldsymbol{\sigma}^{eq} = \boldsymbol{\varepsilon}^{-1}$$

With

$$\mathcal{E}_{ij}[\mathbf{a}] \equiv -\left(\frac{\partial F_i[\mathbf{a}]}{\partial a_j}\right) = -\frac{1}{k_B}\left(\frac{\partial^2 S[\mathbf{a}]}{\partial a_i \partial a_j}\right)$$

(IV) On the structure of the "linear laws":

$$\frac{d\Delta\overline{\mathbf{a}}(t)}{dt} = -\mathcal{L} \circ \sigma^{ss-1} \circ \Delta\overline{\mathbf{a}}(t)$$

(IV) On the structure of the "linear laws":

$$\frac{d\Delta\overline{\mathbf{a}}(t)}{dt} = -\mathcal{L} \circ \sigma^{ss-1} \circ \Delta\overline{\mathbf{a}}(t)$$

$$= -L \cdot \varepsilon \cdot \Delta a(t)$$

(IV) On the structure of the "linear laws":

$$\frac{d\Delta\overline{\mathbf{a}}(t)}{dt} = -\mathcal{L} \circ \sigma^{ss-1} \circ \Delta\overline{\mathbf{a}}(t)$$

$$= -L \cdot \varepsilon \cdot \Delta a(t)$$

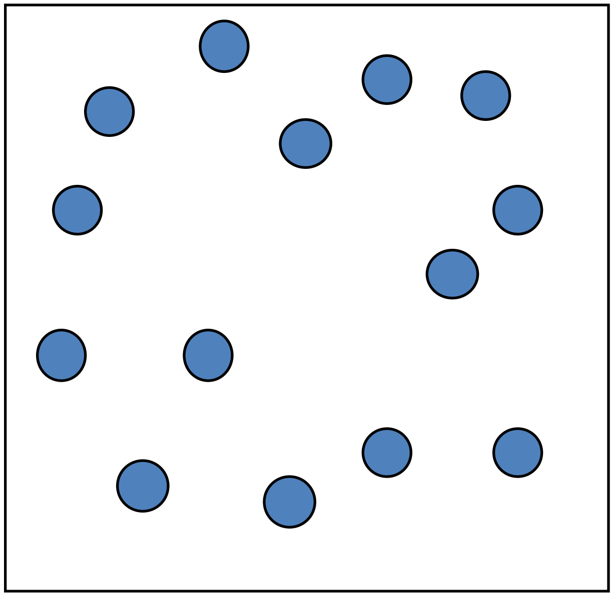
Thus, linear laws of irreversible thermodynamics

$$\boxed{\frac{d\Delta a(t)}{dt} = -L \cdot \Delta F(t)}$$

CONTENT

- Introduction and advanced summary.
- Fundamental principles: (molecular) thermodynamics.
- Fundamental principles: (molecular) Irreversible thermodynamics.
- *Equilibrium* Self-consistent generalized Langevin equation (SCGLE) theory.
- Aging and irreversibility: the NE-SCGLE theory.
- Full exercise: Lennard-Jones—like liquid.
- Perspectives.

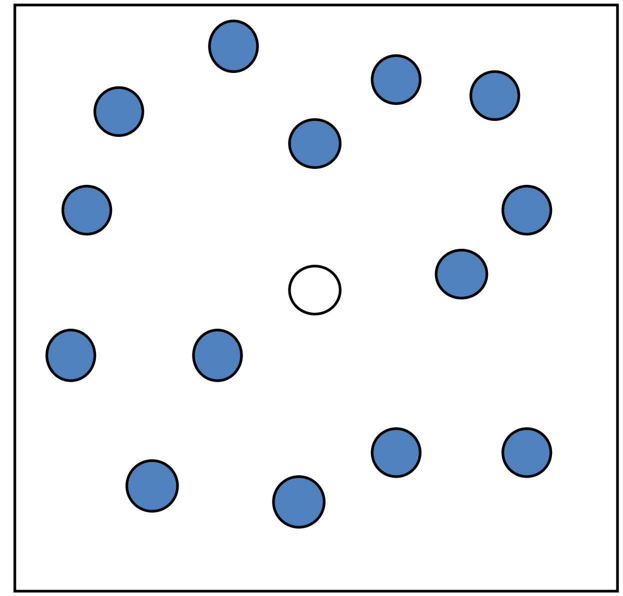
Example: Langevin Equation for N Interacting Brownian Particles



$$M\frac{dV_i(t)}{dt} = -\zeta^0 V_i(t) + f_i^0(t) - \nabla \sum_j u^{eff}(\rho_{ij})$$

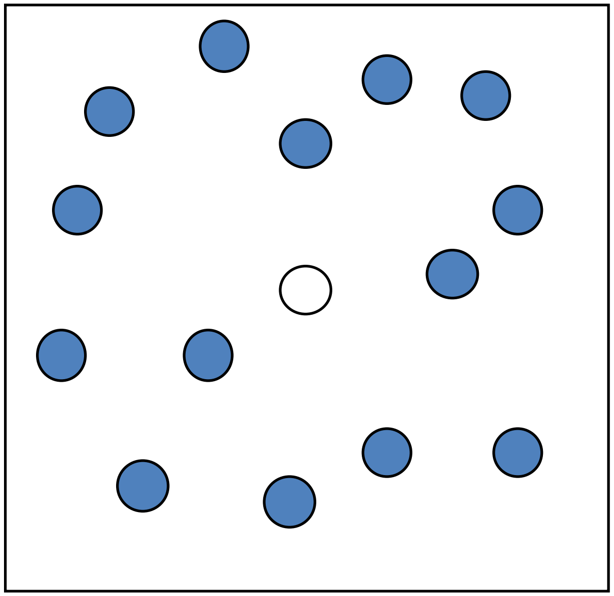
(i=1,2, …, N)

Example: Langevin Equation for N Interacting Brownian Particles



$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t) - \nabla \sum_j u^{eff}(\rho_j)$$

Example: Langevin Equation for Interacting Brownian Particles



$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t) - \nabla \sum_j u^{eff}(\rho_j)$$

$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t) - \int \nabla u^{eff}(\rho) n^*(\rho,t) d^3\rho$$

$$n^*(\rho,t) \equiv \sum_{i=1}^{n} \delta(\rho - \rho_i(t))$$

$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t) - \underline{\int \nabla u^{eff}(\rho)\delta n^*(\vec{\rho},t)}$$

$$\frac{\partial \delta n^*(\vec{\rho},t)}{\partial t} = \underline{\left[\nabla n^{eq}(\rho)\right]\cdot V(t)} + D^0\nabla^2\delta n^*(\vec{\rho},t) + f(r,t)$$

Contraction of the description (eliminate δn*(ρ,t)):

$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t) - \int \nabla u^{eff}(\rho)\delta n^*(\vec{\rho},t)$$

$$\frac{\partial \delta n^*(\vec{\rho},t)}{\partial t} = \left[\nabla n^{eq}(\rho)\right]\cdot V(t) + D^0\nabla^2\delta n^*(\vec{\rho},t) + f(r,t)$$

Contraction of the description (eliminate $\delta n^*(\rho,t)$):

$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t) - \int \Delta\zeta(t-t')V(t')dt' + F(t)$$

Contraction of the description (eliminate $\delta n^*(\rho,t)$):

$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t) - \int \Delta\zeta(t-t')V(t')dt' + F(t)$$

$$\Delta\zeta(t) = \int \left[\nabla u^{eff}(\rho)\right]\chi^*(\vec{\rho},\vec{\rho}';t)\left[\nabla n^{eq}(\rho')\right]d^3\rho\, d^3\rho'$$

Contraction of the description (eliminate $\delta n^*(\rho,t)$):

$$M\frac{dV(t)}{dt} = -\zeta^0 V(t) + f^0(t) - \int \Delta\zeta(t-t')V(t')dt' + F(t)$$

$$\Delta\zeta^*(t) \equiv \frac{\Delta\zeta(t)}{\zeta^0} = \frac{D_0 n}{3(2\pi)^3}\int d^3k \frac{[kh(k)]^2}{S^2(k)} F(k,t)F_S(k,t)$$

F(k,t) describes the decay of density fluctuations

$$F(k,t) \equiv \left\langle \delta n(k,t)\delta n(k,0) \right\rangle$$

Thus, we need

$$\frac{\partial \delta n(k,t)}{\partial t} = ?$$

Physica 146A (1987) 483–505
North-Holland, Amsterdam

THE FLUCTUATION–DISSIPATION THEOREM FOR NON-MARKOV PROCESSES AND THEIR CONTRACTIONS: THE ROLE OF THE STATIONARITY CONDITION

M. MEDINA-NOYOLA*

Fakultät für Physik, Universität Konstanz, D-7750 Konstanz, Fed. Rep. Germany

J.L. DEL RIO-CORREA

Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa, Mexico 13 DF, Mexico

Received 6 May 1987

THEOREM OF STATIONARITY

$$\mathrm{d}\boldsymbol{a}(t)/\mathrm{d}t = -\int_0^t \mathbf{G}(t-t')\boldsymbol{a}(t')\,\mathrm{d}t' + \boldsymbol{f}(t)$$

Theorem A. Let $\boldsymbol{a}(t)$ be an N-dimensional stochastic process defined as the formal solution of the generalized Langevin equation, eq. (3.1), with random initial condition $\boldsymbol{a}(0)$, and with $\boldsymbol{f}(t)$ being an N-dimensional stochastic process, statistically uncorrelated with $\boldsymbol{a}(0)$ for all times t, i.e., such that

$$\langle \boldsymbol{f}(t)\boldsymbol{a}^{\mathrm{T}}(0)\rangle = \langle \boldsymbol{a}(0)\boldsymbol{f}^{\mathrm{T}}(t)\rangle = \mathbf{0}\,. \tag{3.4}$$

Let us also assume that $\langle \boldsymbol{a}(0)\rangle = \langle \boldsymbol{f}(t)\rangle = 0$. Then, the following three statements are equivalent:

(i) $\boldsymbol{a}(t)$ is stationary, i.e.,

$$\langle \boldsymbol{a}(t+s)\boldsymbol{a}^{\mathrm{T}}(t'+s)\rangle = \langle \boldsymbol{a}(t)\boldsymbol{a}^{\mathrm{T}}(t')\rangle\,. \tag{3.5}$$

(ii) $f(t)$ is stationary and $\mathbf{G}(t)$ is such that the generalized Langevin equation has the general structure

$$\mathrm{d}\boldsymbol{a}(t)/\mathrm{d}t = -\boldsymbol{\omega\sigma}^{-1}\boldsymbol{a}(t) - \int_0^t \mathbf{L}(t-t')\boldsymbol{\sigma}^{-1}\boldsymbol{a}(t')\,\mathrm{d}t' + \boldsymbol{f}(t)\,, \tag{3.6}$$

where

$$\boldsymbol{\sigma} \equiv \langle \boldsymbol{a}(0)\boldsymbol{a}^{\mathrm{T}}(0)\rangle\,, \tag{3.7}$$

$\boldsymbol{\omega}$ is a time-independent antisymmetric matrix,

$$\boldsymbol{\omega} = -\boldsymbol{\omega}^{\mathrm{T}}\,, \tag{3.8}$$

and $\mathbf{L}(t)$ is given by

$$\mathbf{L}(t) = \mathbf{L}^{\mathrm{T}}(-t) = \langle \boldsymbol{f}(t)\boldsymbol{f}^{\mathrm{T}}(0)\rangle\,. \tag{3.9}$$

Fundamental vs. Phenomenological

- Generalized Langevin Equation

$$\mathbf{a}(t) = \left(a_1(t), a_2(t), \cdots, a_n(t)\right)$$

$$\frac{d\mathbf{a}(t)}{dt} = -\mathbf{w}\cdot\sigma^{-1}\cdot\mathbf{a}(t) - \int_0^t \mathbf{L}(t-t')\cdot\sigma^{-1}\cdot\mathbf{a}(t')dt' + \mathbf{f}(t)$$

- "Rigorous" point of view (Kirkwood, Mori, Zwanzig, ….)

- "Phenomenological" point of view (Langevin, Onsager, Fox-Uhlenbeck, Keizer, …)

F(k,t) describes the decay of density fluctuations

$$F(k,t) \equiv \langle \delta n(k,t)\delta n(k,0) \rangle$$

Thus, we need

$$\frac{\partial \delta n(k,t)}{\partial t} = ?$$

$$F(k,z) = \frac{S(k)}{z + \dfrac{k^2 D_0 S^{-1}(k)}{1 + C(k,z)}}$$

Self-consistent generalized Langevin equation (SCGLE) theory

$$\Delta\zeta(t) = \frac{Do}{3(2\pi^3)n}\int d^3k\left[\frac{k[S(k)-1]}{S(k)}\right]^2 F(k,t)F_S(k,t)$$

$$F(k,z) = \frac{S(k)}{z + \frac{k^2 D_0 S^{-1}(k)}{1+\lambda(k)\Delta\zeta(z)}},$$

$$F_S(k,z) = \frac{1}{z + \frac{k^2 D_0}{1+\lambda(k)\Delta\zeta(z)}},$$

$$\lambda(k) = \frac{1}{1+(k/k_{min})^2}.$$

(PRE **67**: 021108(2003); PRE **76**: 062502 (2007))

EQUILIBRIUM SCGLE THEORY

Equilibrium Structure S(k)

$$\hat{F}(k,z;t) = \frac{S(k;t)}{z + \frac{k^2 D^0 S^{-1}(k;t)}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

$$\hat{F}_S(k,z;t) = \frac{1}{z + \frac{k^2 D^0}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

$$\Delta\zeta^*(\tau;t) = \frac{D_0}{3\,(2\pi)^3\,\overline{n}^{(f)}} \int d\mathbf{k}\ k^2 \left[\frac{S(k;t)-1}{S(k;t)}\right]^2 F(k,\tau;t) F_S(k,\tau;t).$$

Equilibrium Dynamic Properties

MODE COUPLING THEORY

Equilibrium Structure S(k)

$$\hat{F}(k,z;t) = \frac{S(k;t)}{z + \frac{k^2 D^0 S^{-1}(k;t)}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

$$\hat{F}_S(k,z;t) = \frac{1}{z + \frac{k^2 D^0}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

$$\Delta\zeta^*(\tau;t) = \frac{D_0}{3\,(2\pi)^3\,\overline{n}^{(f)}} \int d\mathbf{k}\; k^2 \left[\frac{S(k;t)-1}{S(k;t)}\right]^2 F(k,\tau;t)F_S(k,\tau;t).$$

Equilibrium Dynamic Properties

CONTENT

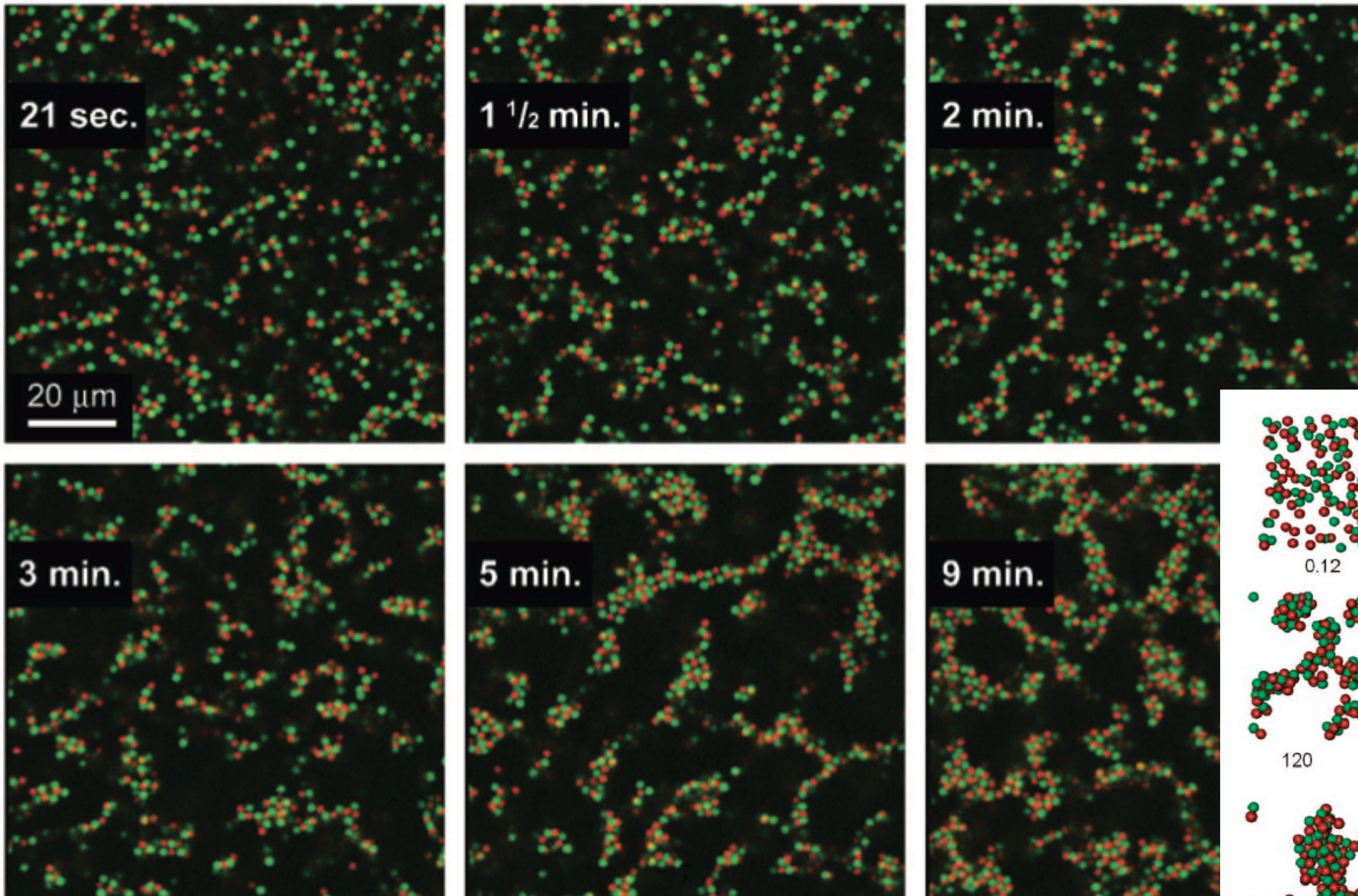
- Introduction and advanced summary.
- Fundamental principles: (molecular) thermodynamics.
- Fundamental principles: (molecular) Irreversible thermodynamics.
- *Equilibrium* Self-consistent generalized Langevin equation (SCGLE) theory.
- Aging and irreversibility: the NE-SCGLE theory.
- Full exercise: Lennard-Jones—like liquid.
- Perspectives.

Gel Formation in Suspensions of Oppositely Charged Colloids: Mechanism and Relation to the Equilibrium Phase Diagram

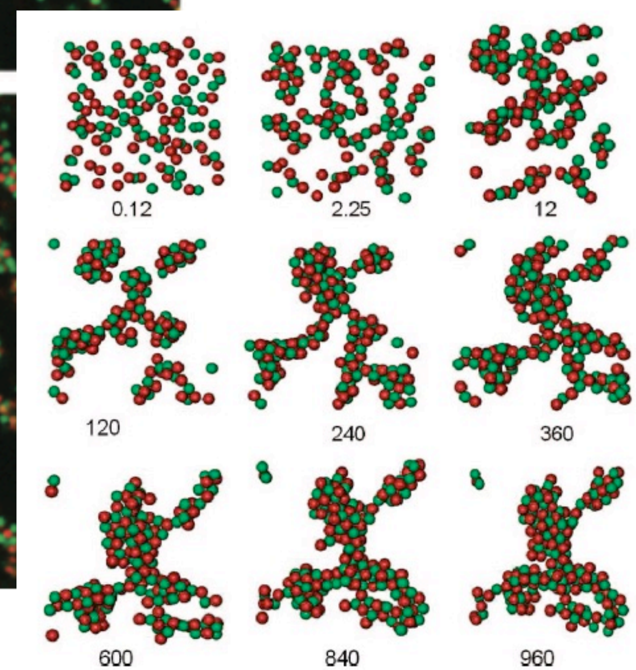
Eduardo Sanz, Mirjam E. Leunissen, Andrea Fortini, Alfons van Blaaderen, and Marjolein Dijkstra

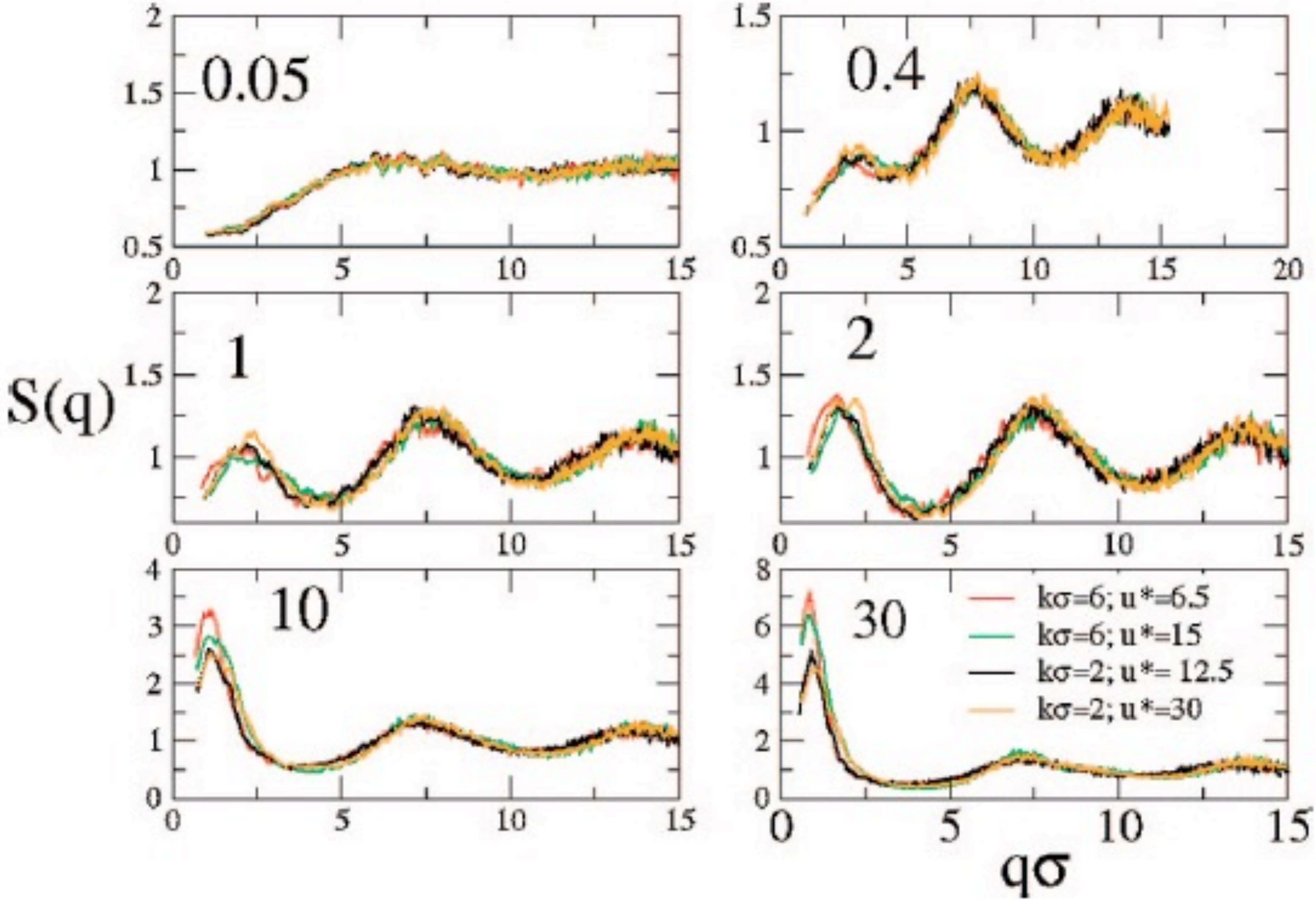
J. Phys. Chem. B, **2008**, 112 (35), 10861-10872 • DOI: 10.1021/jp801440v • Publication Date (Web): 08 August 2008

Experiments:



Simulations:




0.05
0.4
1
2
10
30
S(q)
qσ
kσ=6; u*=6.5
kσ=6; u*=15
kσ=2; u*= 12.5
kσ=2; u*=30

$$\boxed{\frac{\partial S(k;t_w)}{\partial t_w} = ?}$$

Onsager's Linear Irreversible Thermodynamics

$$\frac{d\Delta a(t)}{dt} = -L \cdot \Delta F(t)$$

1968 Chemistry Nobel Laureate

Onsager's Linear Irreversible Thermodynamics

$$\frac{d\Delta a(t)}{dt} = -L \cdot \Delta F(t)$$

¡Provides universal and fundamental basis!

$$\frac{d\Delta a(t)}{dt} = -L \cdot \Delta F(t)$$

Stationary solutions:

$$\frac{d\Delta a(t)}{dt} = -L \cdot \Delta F(t)$$

Stationary solutions:

Thermodynamic Equilibrium states:

$$\Delta F(t) = 0$$

$$\frac{d\Delta a(t)}{dt} = -L \cdot \Delta F(t)$$

Stationary solutions:

Thermodynamic Equilibrium states:

$$\Delta F(t) = 0$$

Dynamically arrested states:

$$L = 0$$

WE EXTENDED
ONSAGER'S THEORY OF THERMAL FLUCTUATIONS TO

NON-STATIONARY AND
NON-EQUILIBRIUM CONDITIONS

THE RESULTING NON-EQUILIBRIUM THEORY:

TIME-EVOLUTION EQUATIONS FOR

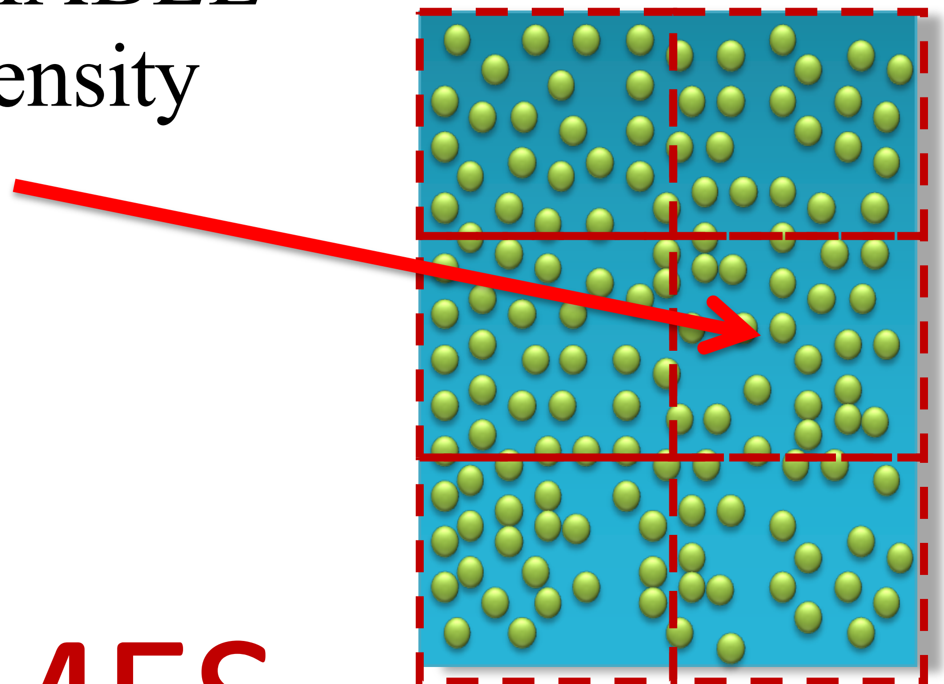
(I) THE MEAN VALUE

(II) THE COVARIANCE

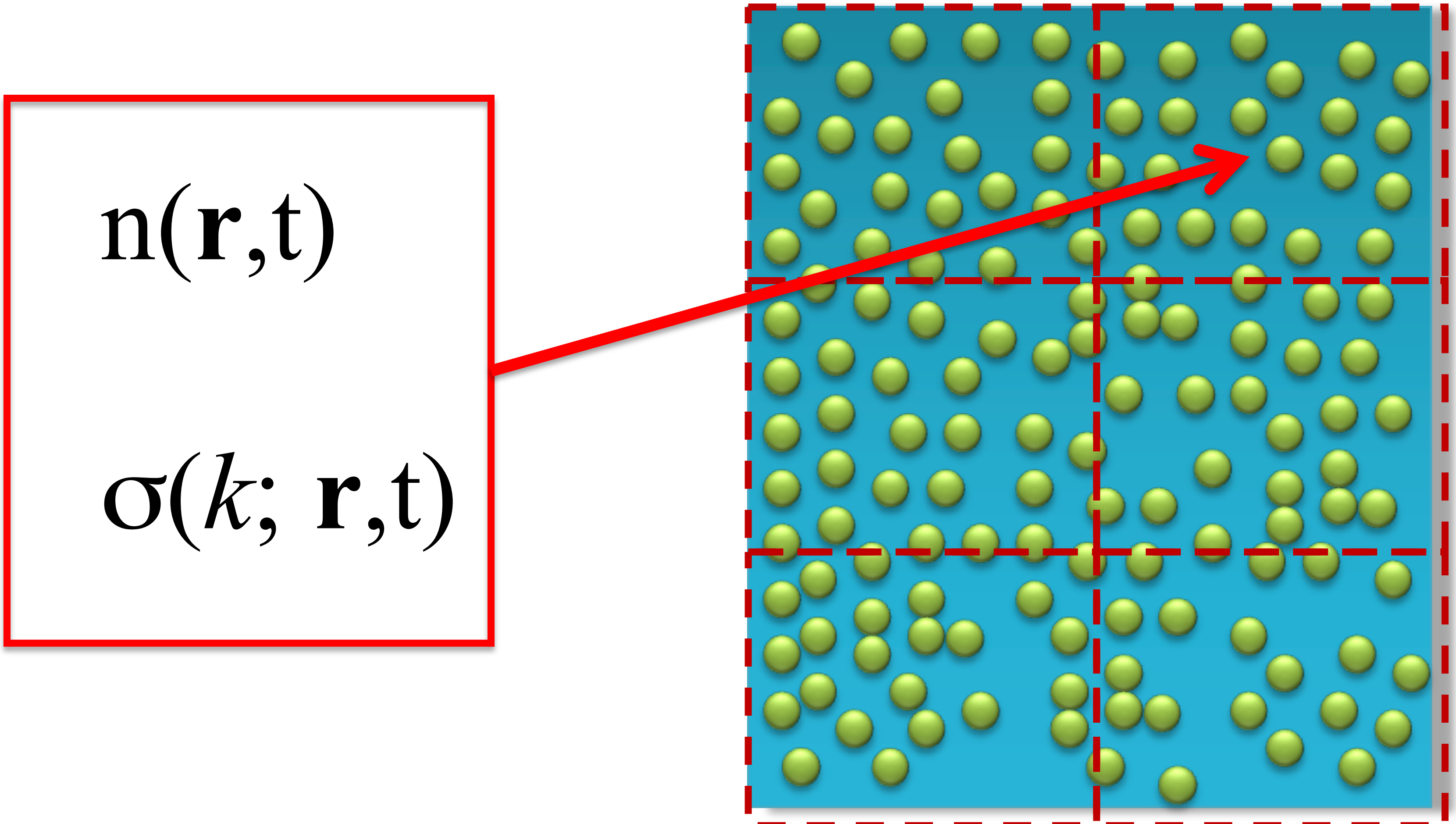
APPLIED TO THE VARIABLE

$\mathbf{n(r,t)}$ = Local number density

OF A LIQUID, …



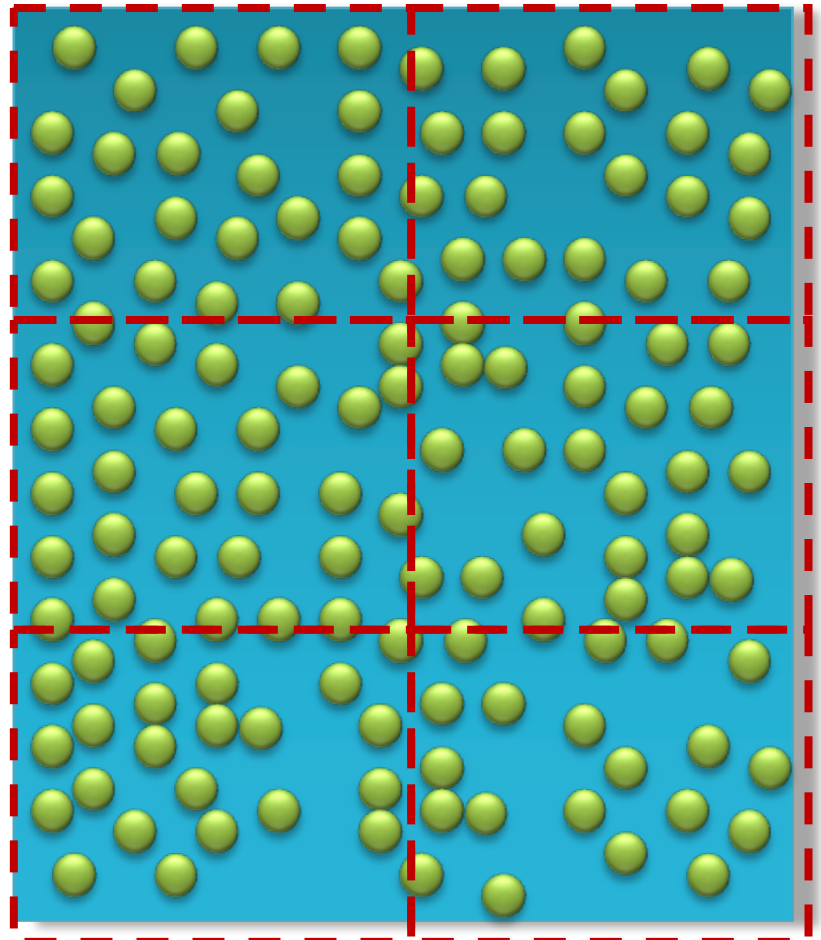
…IT BECOMES A GENERIC THEORY OF LIQUIDS


$n(\mathbf{r},t)$
$\sigma(k;\,\mathbf{r},t)$

$$\frac{\partial \overline{n}(\mathbf{r},t)}{\partial t} = D^0 \nabla \cdot b(\mathbf{r},t)\overline{n}(\mathbf{r},t)\nabla \beta\mu[\mathbf{r};\overline{n}(t)]$$

$n(\mathbf{r},t)$

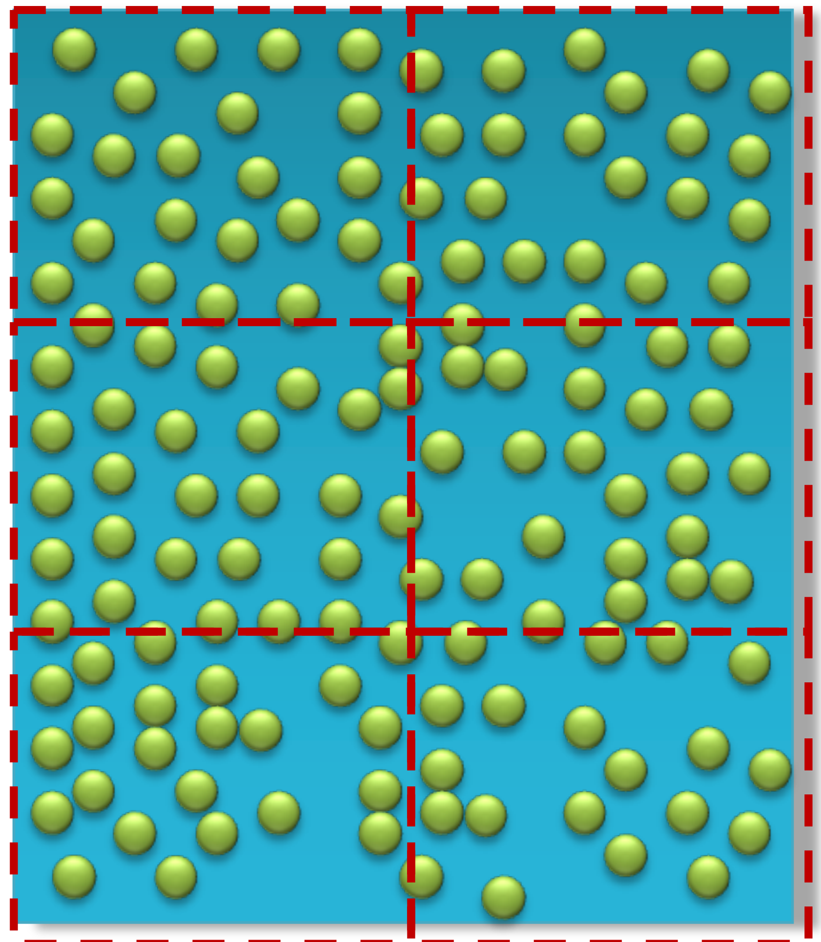
$\sigma(k;\ \mathbf{r},t)$



$$\frac{\partial \sigma(k;\mathbf{r},t)}{\partial t} = -\,2k^2 D^0 \overline{n}(\mathbf{r},t) b(\mathbf{r},t) \mathcal{E}(k;\overline{n}(\mathbf{r},t))\sigma(k;\mathbf{r},t) + 2k^2 D^0 \overline{n}(\mathbf{r},t)\; b(\mathbf{r},t),$$

$n(\mathbf{r},t)$

$\sigma(k;\,\mathbf{r},t)$



$$\frac{\partial \overline{n}(\mathbf{r},t)}{\partial t} = D^0 \nabla \cdot b(\mathbf{r},t)\overline{n}(\mathbf{r},t)\nabla \beta\mu[\mathbf{r};\overline{n}(t)]$$

$$\begin{aligned}\frac{\partial \sigma(k;\mathbf{r},t)}{\partial t} =& -2k^2 D^0 \overline{n}(\mathbf{r},t) b(\mathbf{r},t)\mathcal{E}(k;\overline{n}(\mathbf{r},t))\sigma(k;\mathbf{r},t) \\ & + 2k^2 D^0 \overline{n}(\mathbf{r},t)\ b(\mathbf{r},t),\end{aligned}$$

Estrategy: write

$$n(\mathbf{r},t) = n + \Delta n(\mathbf{r},t),$$

$$b(\mathbf{r},t) = b(t) + \Delta b(\mathbf{r},t),$$

and start by neglecting

$\Delta n(\mathbf{r},t)$ y $\Delta b(\mathbf{r},t)$

FOR UNIFORM SYSTEM ONLY THE EQUATION FOR THE COVARIANCE REMAINS

$$\frac{\partial S(k;t)}{\partial t} = -2k^2 D^0 b(t) \bar{n} \mathscr{E}^{(f)}(k) \left[S(k;t) - 1/\bar{n} \mathscr{E}^{(f)}(k) \right]$$

FOR UNIFORM SYSTEM ONLY THE EQUATION FOR THE COVARIANCE REMAINS

$$\frac{\partial S(k;t)}{\partial t} = -2k^2 D^0 b(t) \bar{n}\mathscr{E}^{(f)}(k) \left[S(k;t) - 1/\bar{n}\mathscr{E}^{(f)}(k) \right]$$

$$\frac{\partial S(k;t)}{\partial t} = -2k^2 D^0 b(t)\overline{n}\mathscr{E}^{(f)}(k)\left[S(k;t) - 1/\overline{n}\mathscr{E}^{(f)}(k)\right]$$

TWO KINDS OF STATIONARY STATES:

$$\frac{\partial S(k;t)}{\partial t} = -2k^2 D^0 b(t)\overline{n}\mathcal{E}^{(f)}(k)\left[S(k;t) - 1/\overline{n}\mathcal{E}^{(f)}(k)\right]$$

TWO KINDS OF STATIONARY STATES:

(I). EQUILIBRIUM STATES:

$$\lim_{t\to\infty}\ [S(k;t) - 1/\overline{n}\mathcal{E}^{(f)}(k)] = 0$$

$$\frac{\partial S(k;t)}{\partial t} = -2k^2 D^0 b(t) \bar{n} \mathscr{E}^{(f)}(k) \left[S(k;t) - 1/\bar{n}\mathscr{E}^{(f)}(k) \right]$$

TWO KINDS OF STATIONARY STATES:

(I). EQUILIBRIUM STATES:

$$\lim_{t\to\infty} \left[S(k;t) - 1/\bar{n}\mathcal{E}^{(f)}(k) \right] = 0$$

(II). ARRESTED STATES:

$$b(\mathrm{t}) \longrightarrow 0$$

S(k;t)

$$\frac{\partial S(k;t)}{\partial t} = -2k^2 D^0 b(t)\overline{n}\mathscr{E}^{(f)}(k)\left[S(k;t) - 1/\overline{n}\mathscr{E}^{(f)}(k)\right]$$

b(t)

NON-EQUILIBRIUM SCGLE THEORY

S(k;t)

$$\frac{\partial S(k;t)}{\partial t} = -2k^2 D^0 b(t) \overline{n} \mathscr{E}^{(f)}(k) \left[S(k;t) - 1/\overline{n}\mathscr{E}^{(f)}(k) \right]$$

b(t)

NON-EQUILIBRIUM SCGLE THEORY

S(k;t)

$$\frac{\partial S(k;t)}{\partial t} = -2k^2 D^0 b(t) \overline{n} \mathscr{E}^{(f)}(k) \left[S(k;t) - 1/\overline{n}\mathscr{E}^{(f)}(k) \right]$$

$$\hat{F}(k,z;t) = \frac{S(k;t)}{z + \frac{k^2 D^0 S^{-1}(k;t)}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

$$\hat{F}_S(k,z;t) = \frac{1}{z + \frac{k^2 D^0}{1+\lambda(k)\ \Delta\hat{\zeta}^*(z;t)}}.$$

$$\Delta\zeta^*(\tau;t) = \frac{D_0}{3(2\pi)^3 \overline{n}^{(f)}} \int d\mathbf{k}\ k^2 \left[\frac{S(k;t)-1}{S(k;t)} \right]^2 F(k,\tau;t) F_S(k,\tau;t).$$

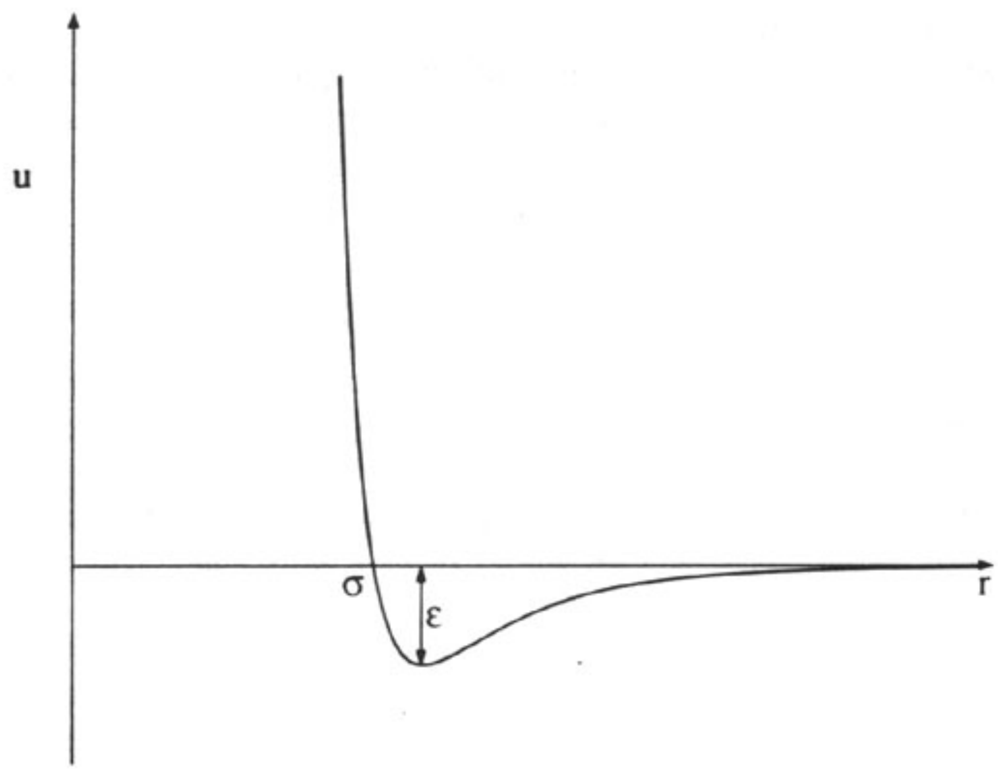
b(t)

CONTENT

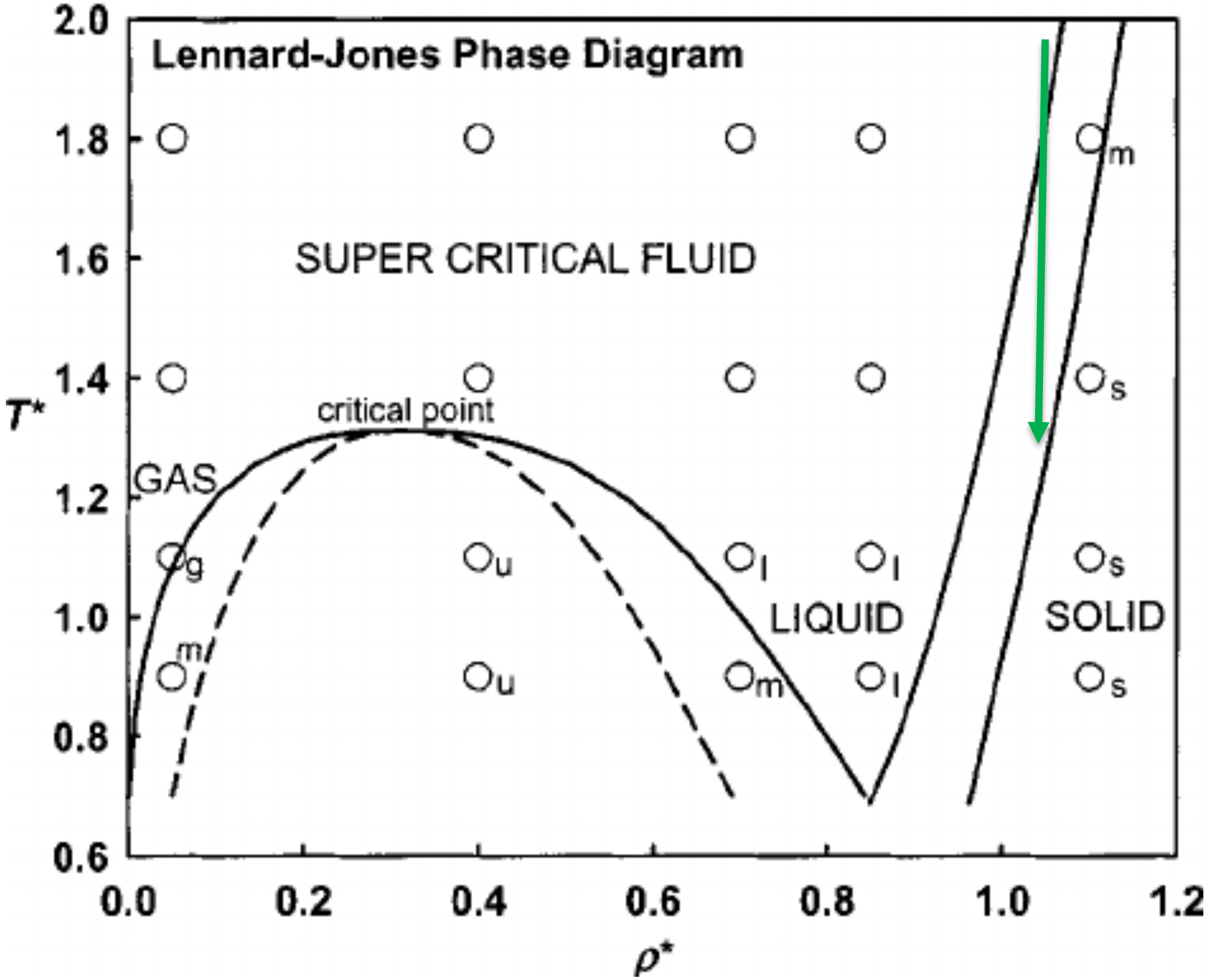
- Introduction and advanced summary.
- Fundamental principles: (molecular) thermodynamics.
- Fundamental principles: (molecular) Irreversible thermodynamics.
- *Equilibrium* Self-consistent generalized Langevin equation (SCGLE) theory.
- Aging and irreversibility: the NE-SCGLE theory.
- Full exercise: Lennard-Jones—like liquid.
- Perspectives.

FLUIDO DE LENNARD-JONES

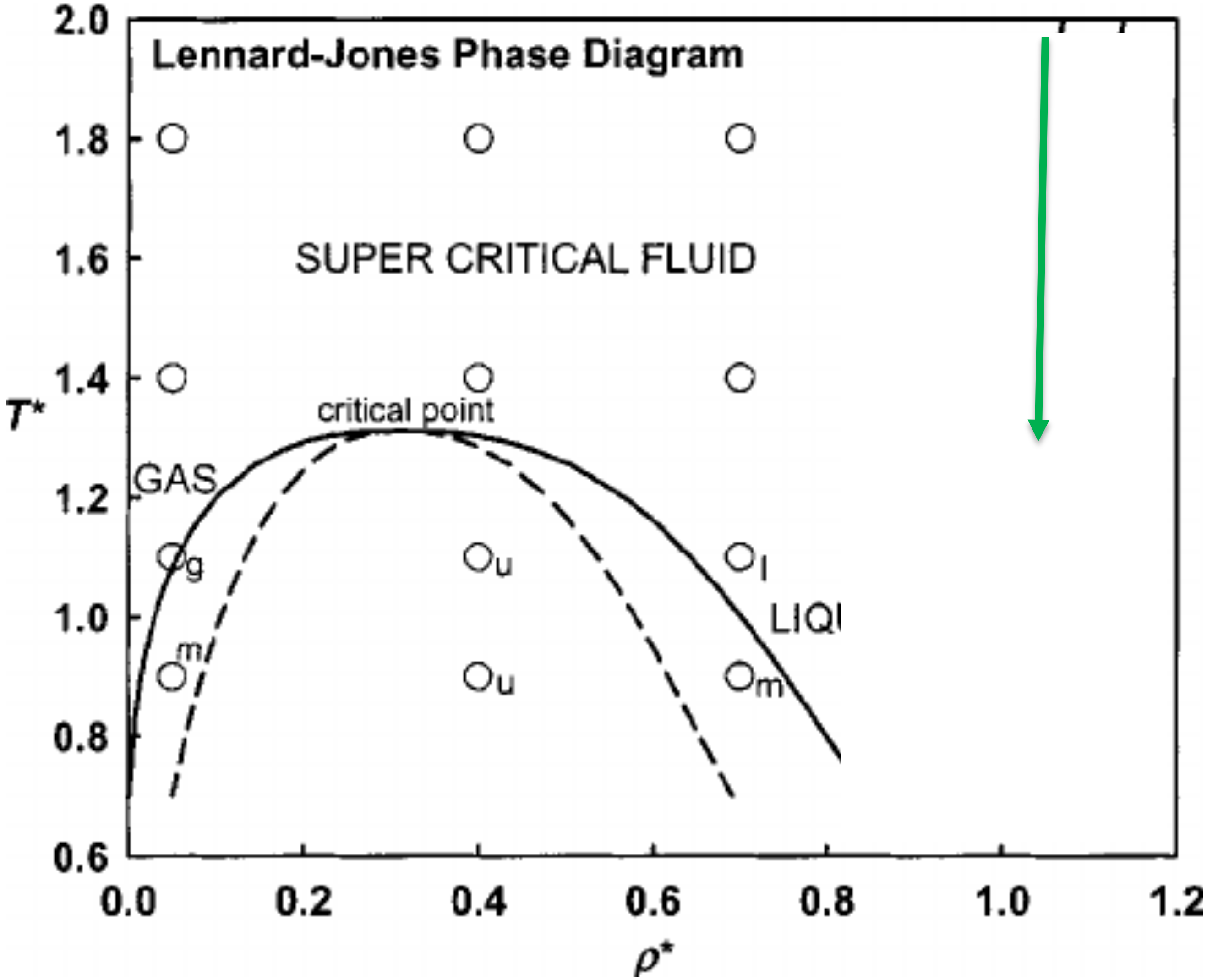
$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



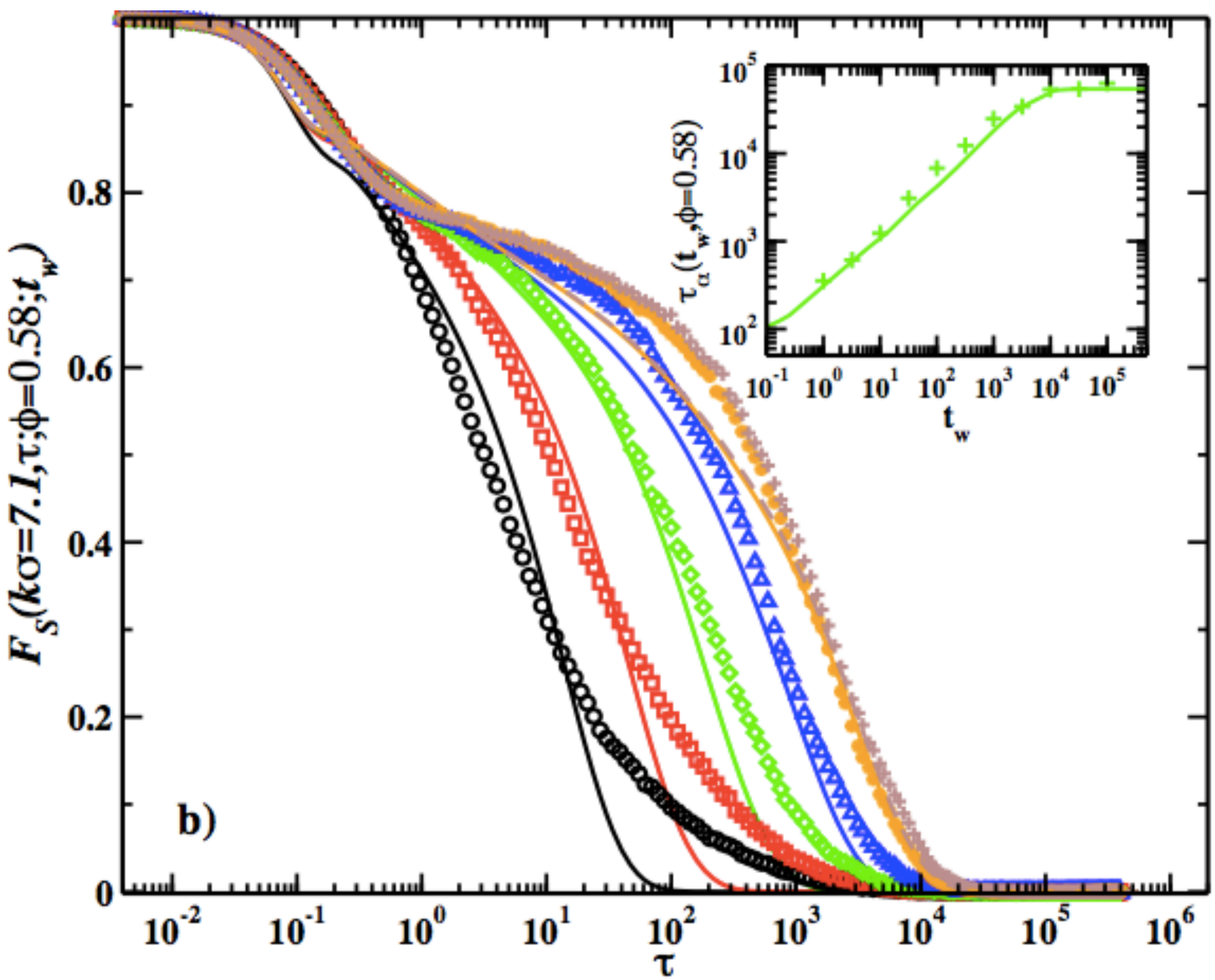
Quenching a dense LJ liquid:



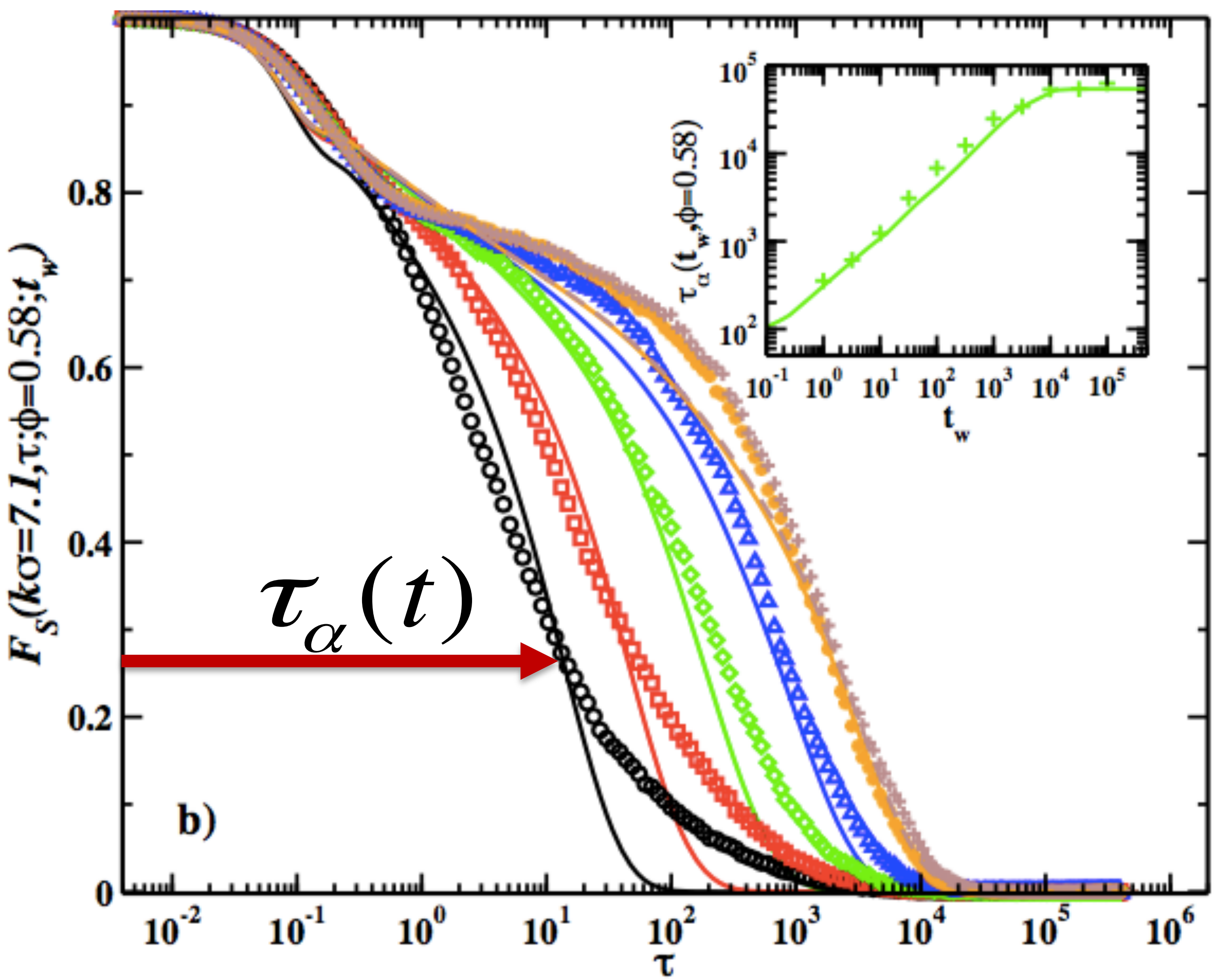
Quenching a dense LJ liquid:



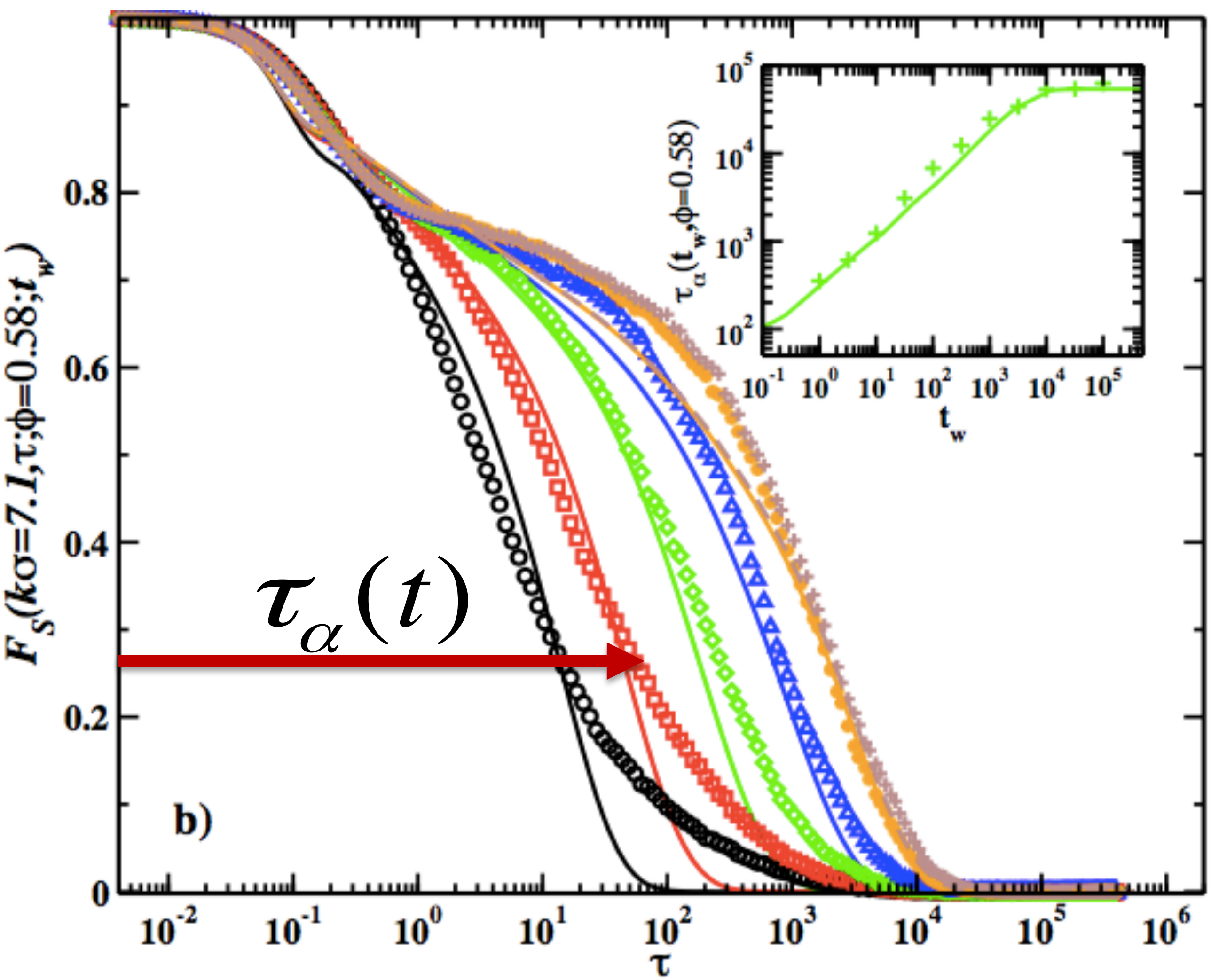
EQUILIBRATION



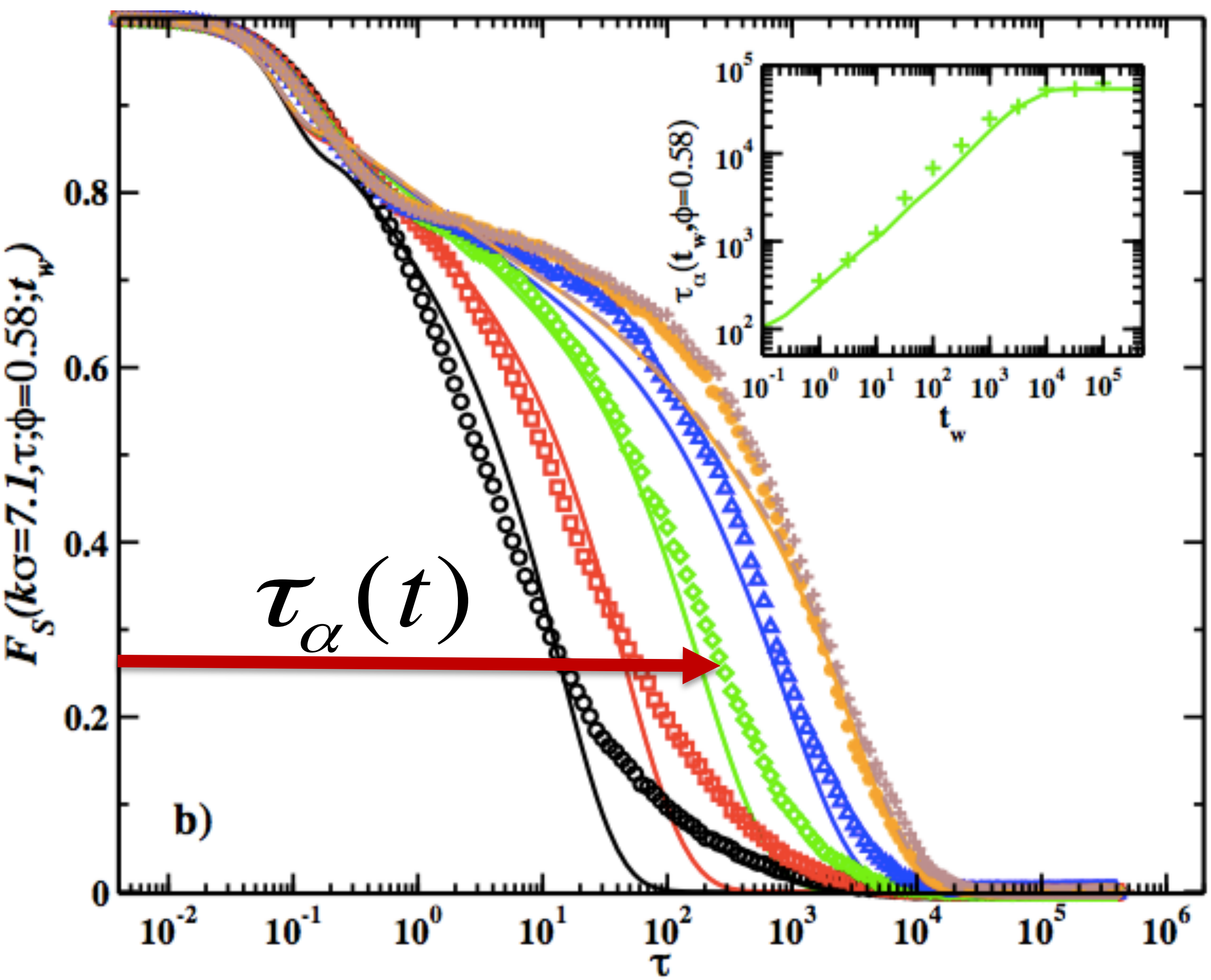
EQUILIBRATION

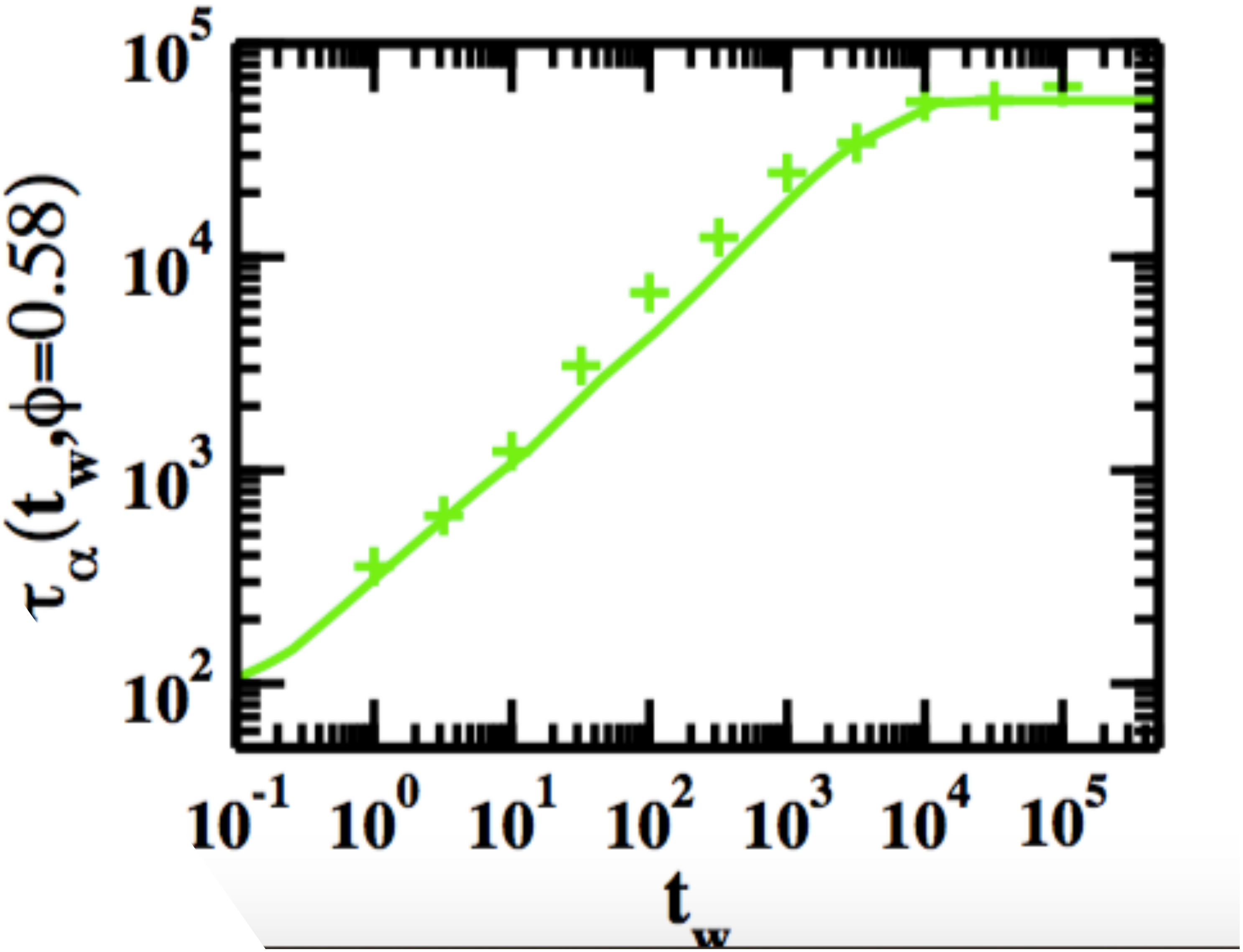


EQUILIBRATION



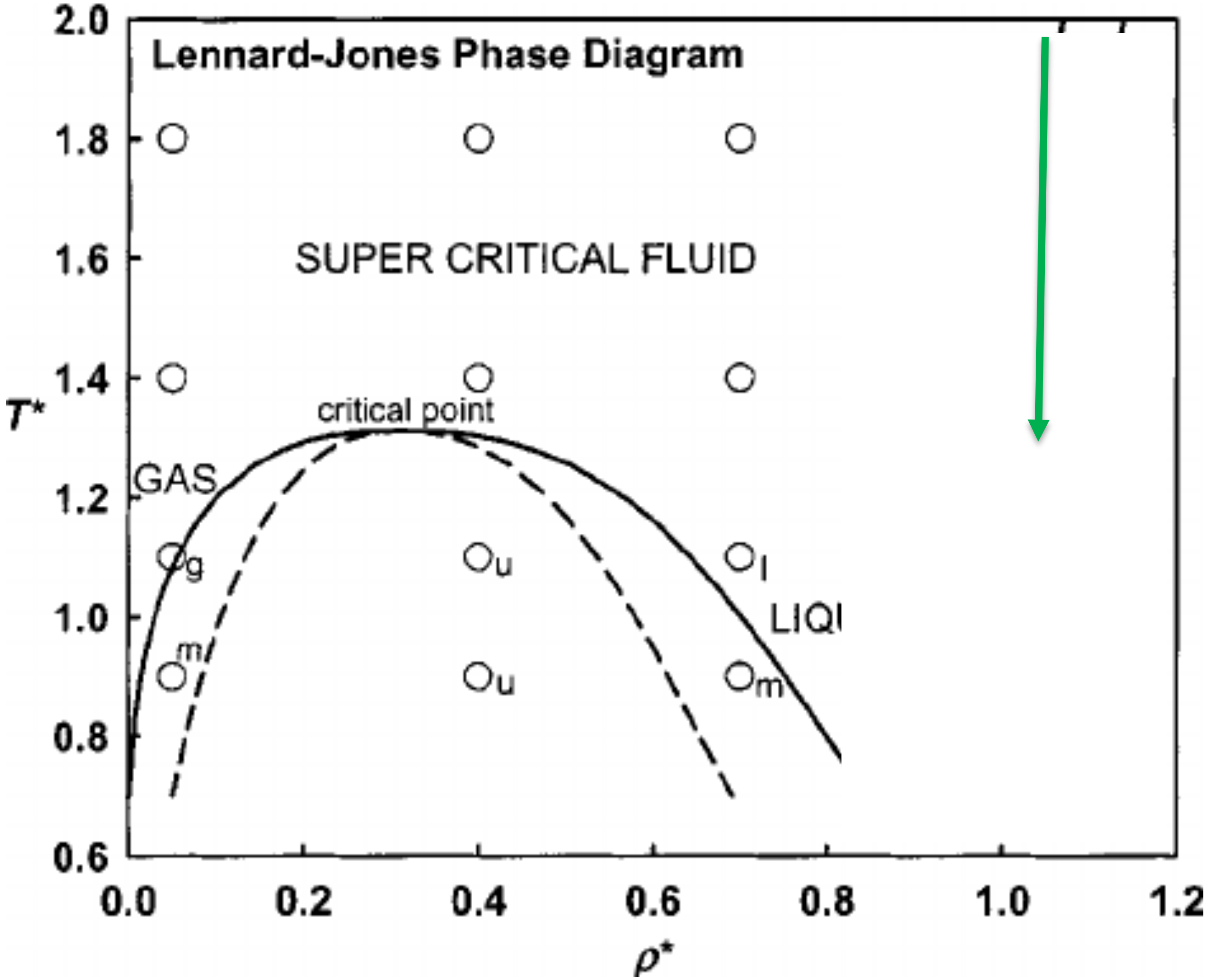
EQUILIBRATION



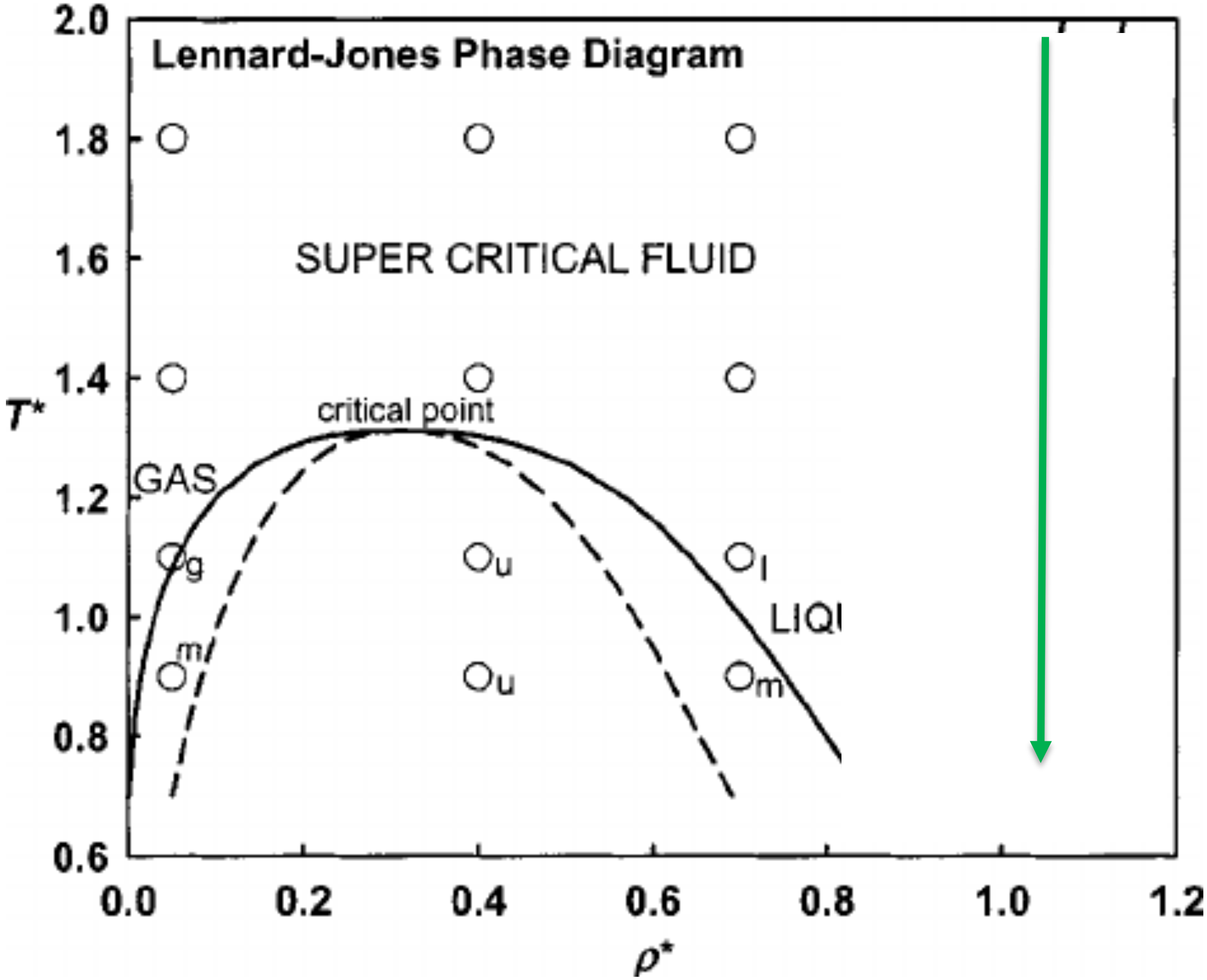


$\tau_\alpha(t_w,\phi=0.58)$
10^5
10^4
10^3
10^2
10^{-1} 10^0 10^1 10^2 10^3 10^4 10^5
t_w

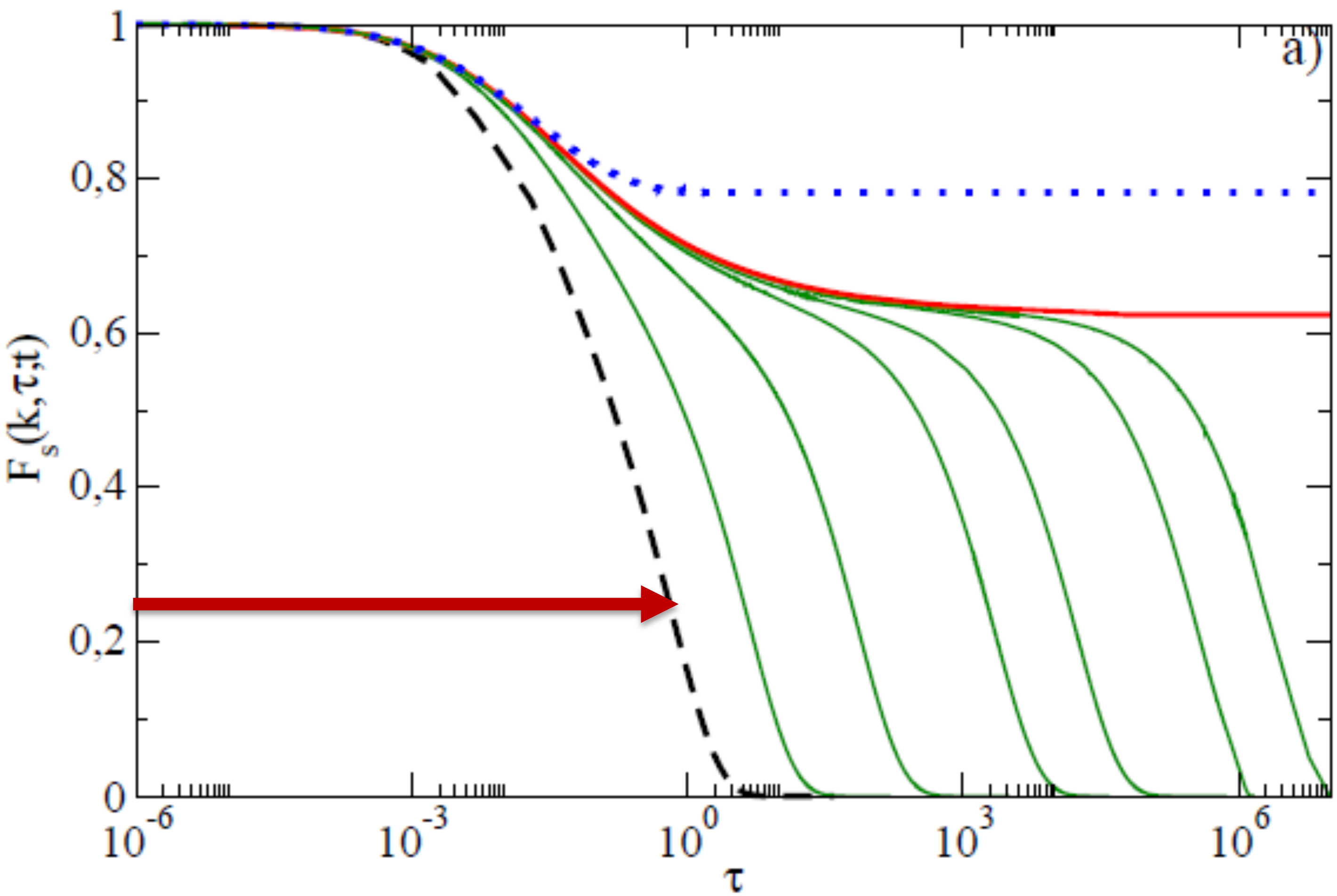
Quenching a dense LJ liquid:



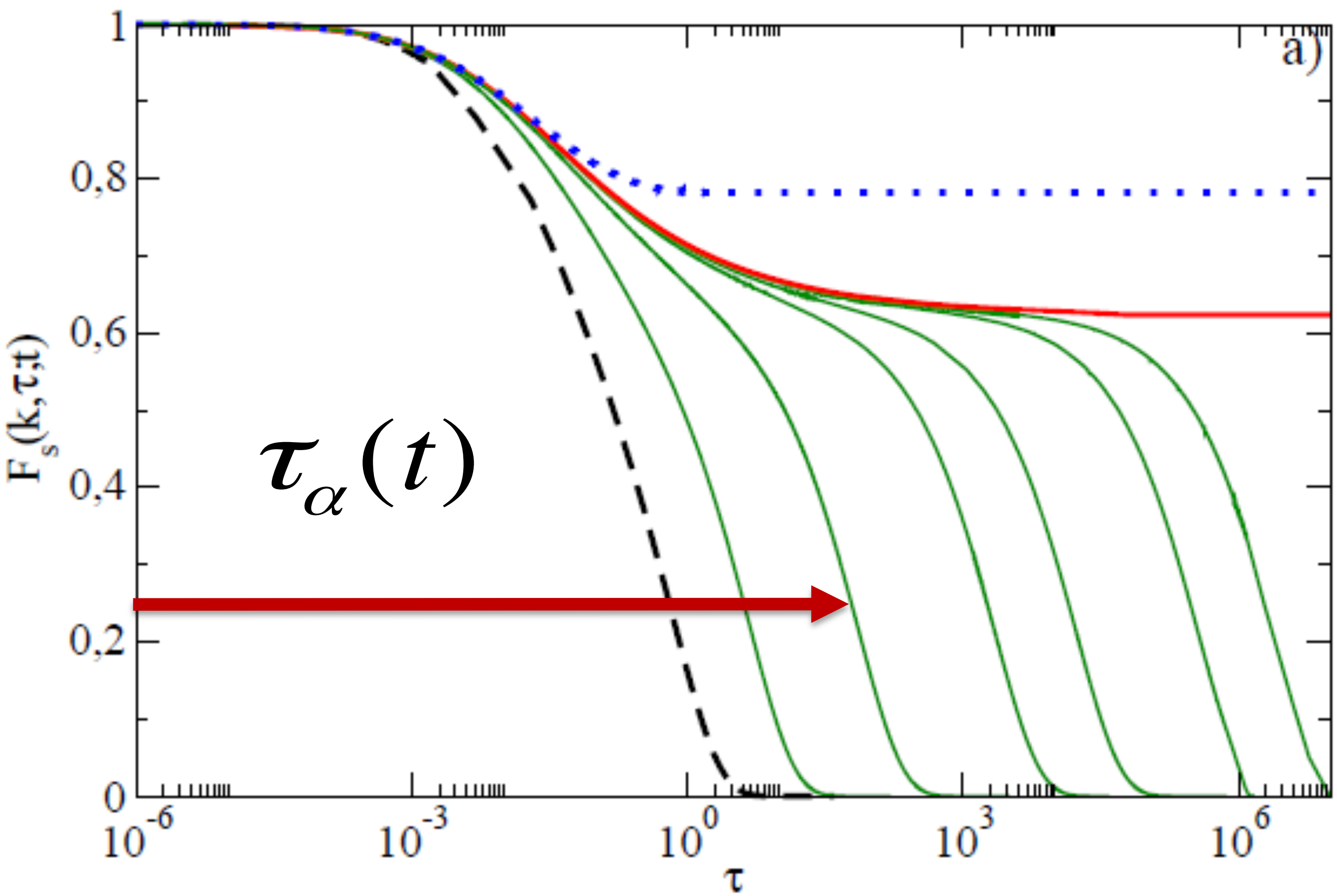
Quenching a dense LJ liquid:



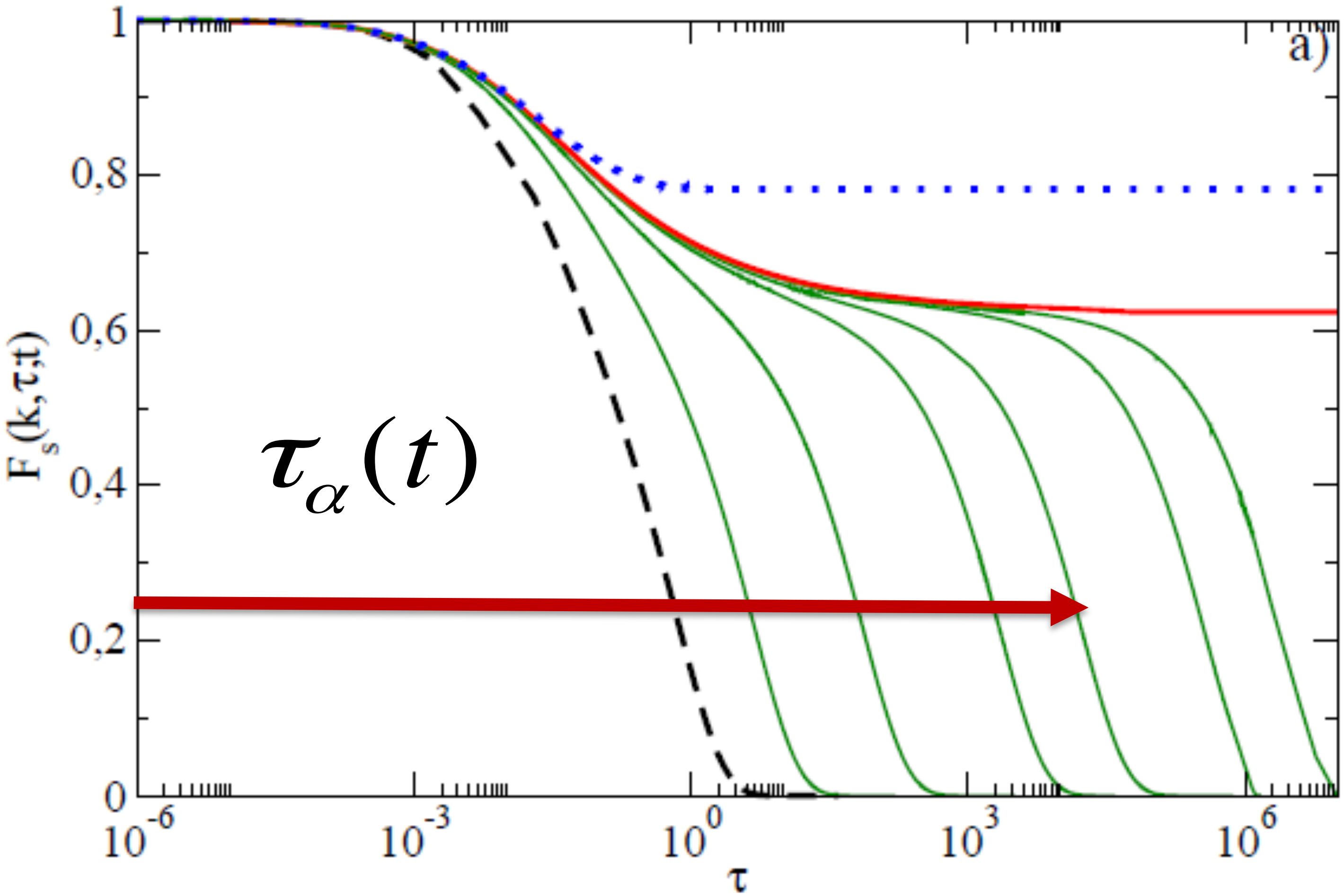
Aging of time-dependent correlations



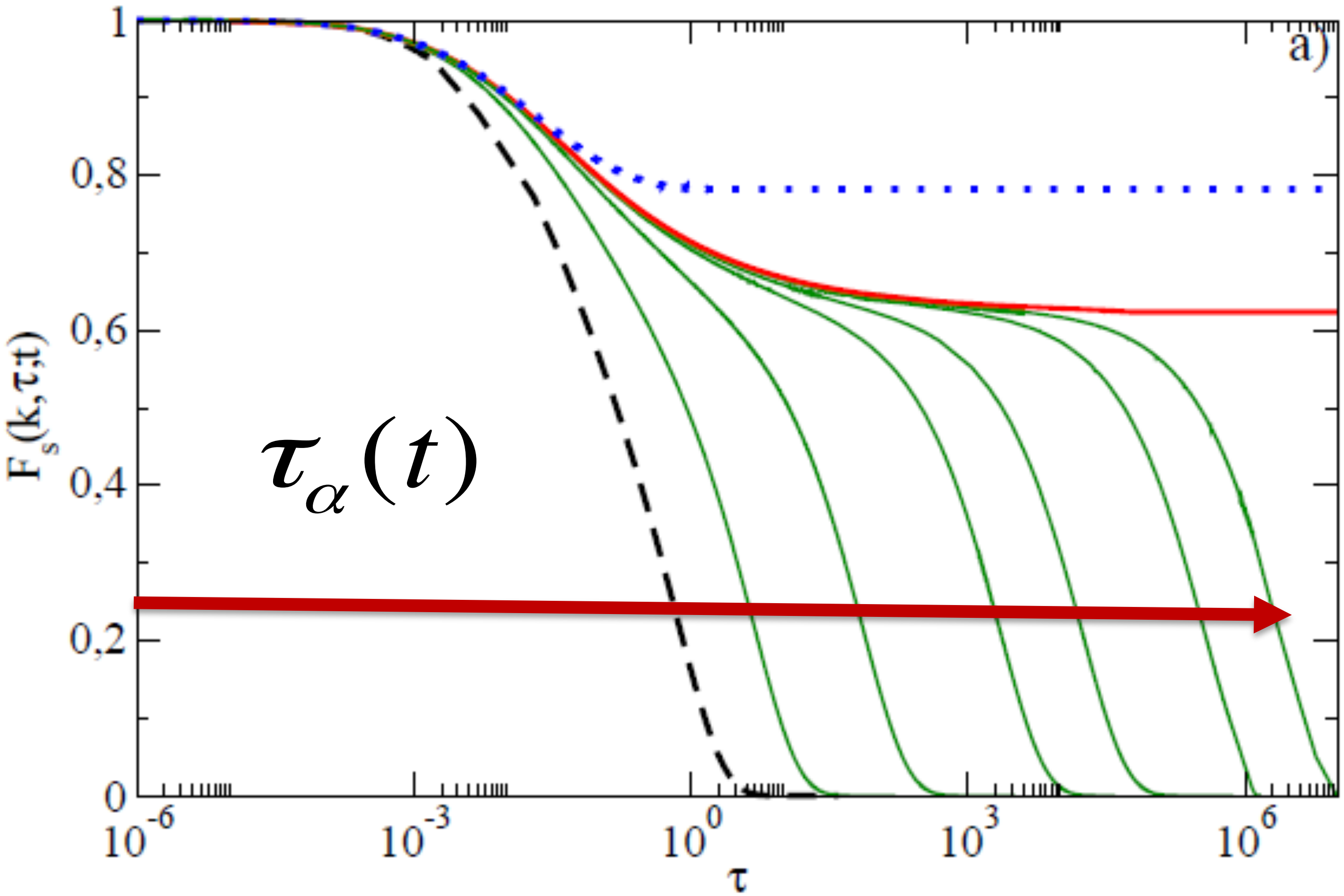
Aging of time-dependent correlations



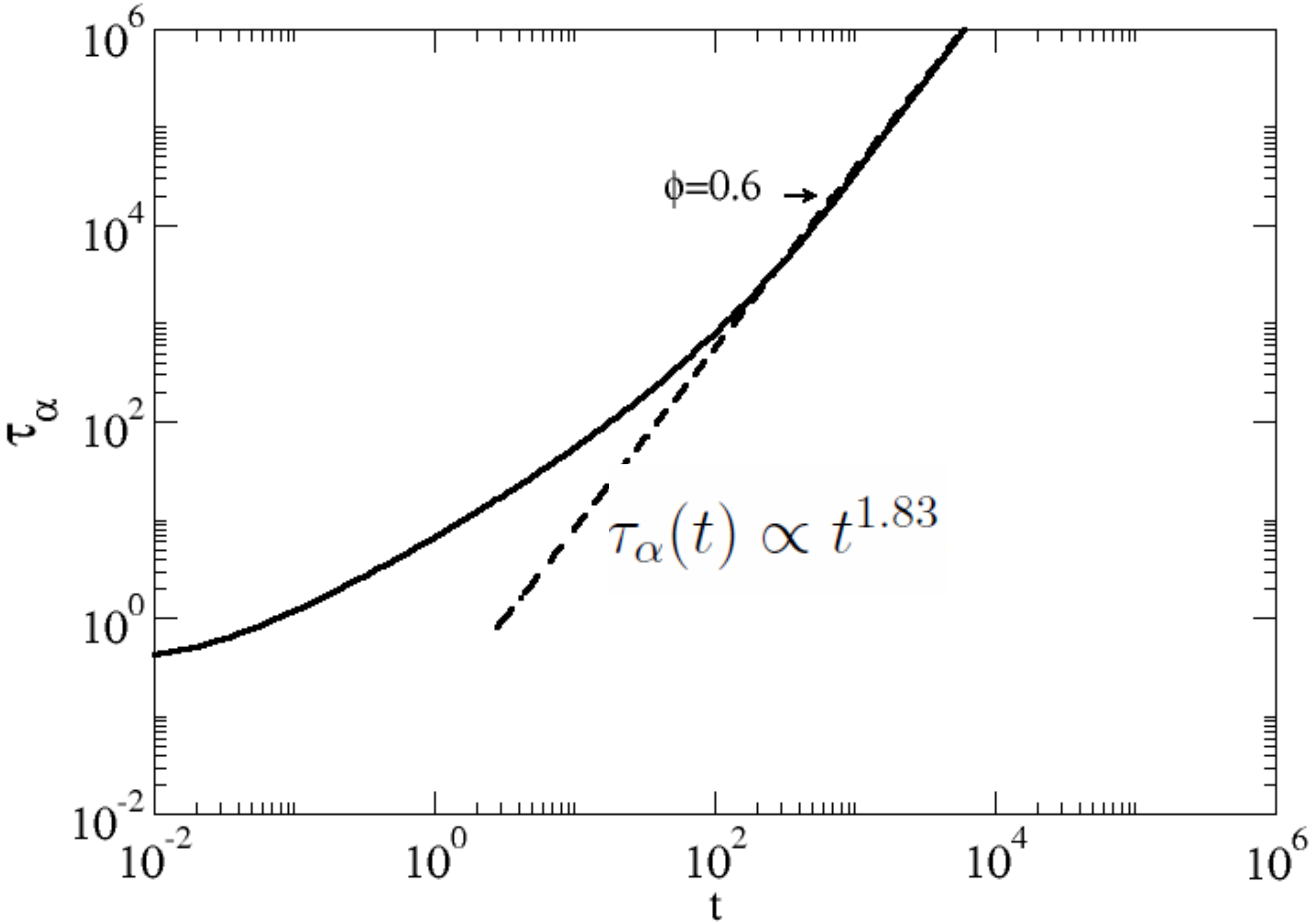
Aging of time-dependent correlations



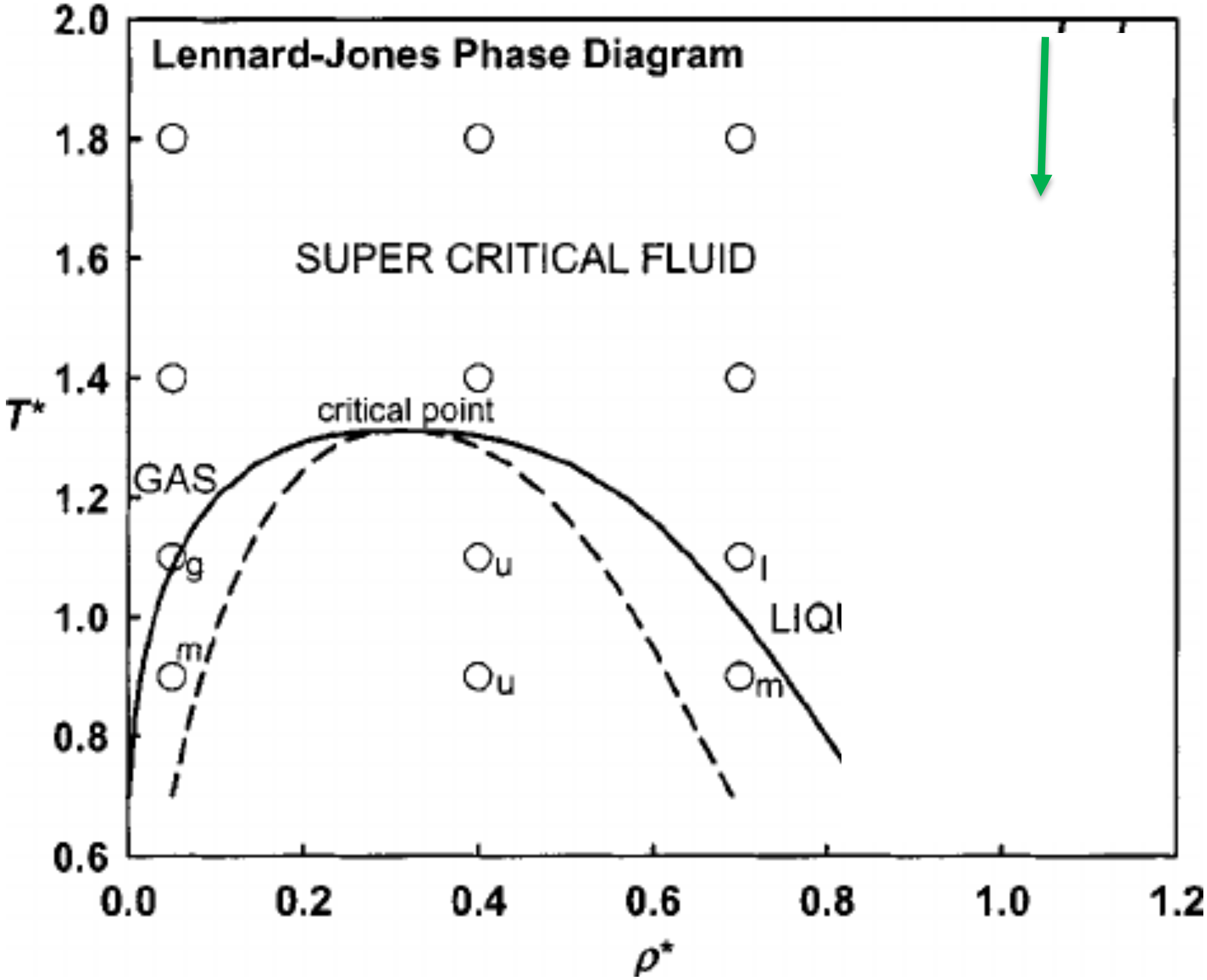
Aging of time-dependent correlations



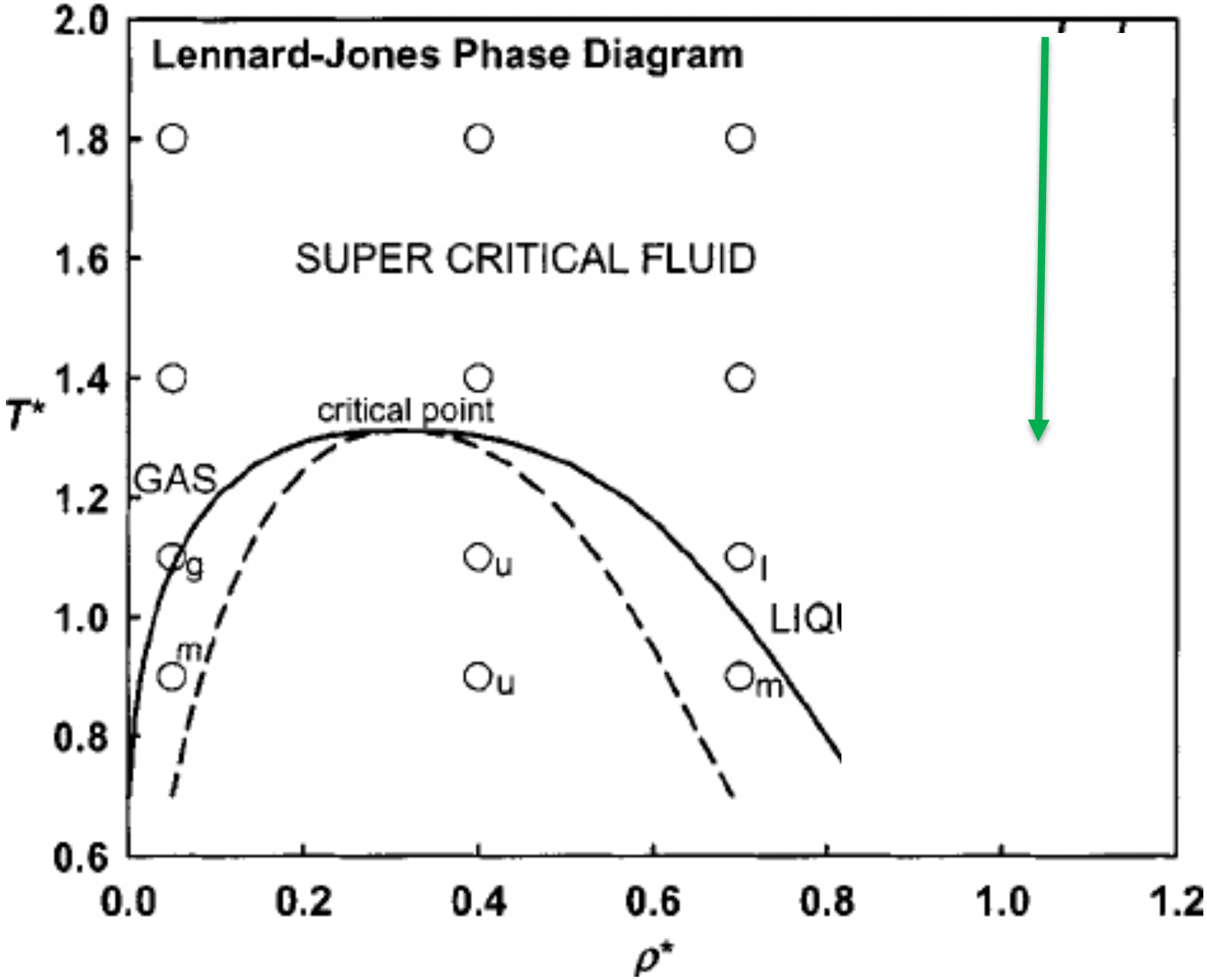
Alpha-Relaxation Time as a Function of Waiting Time



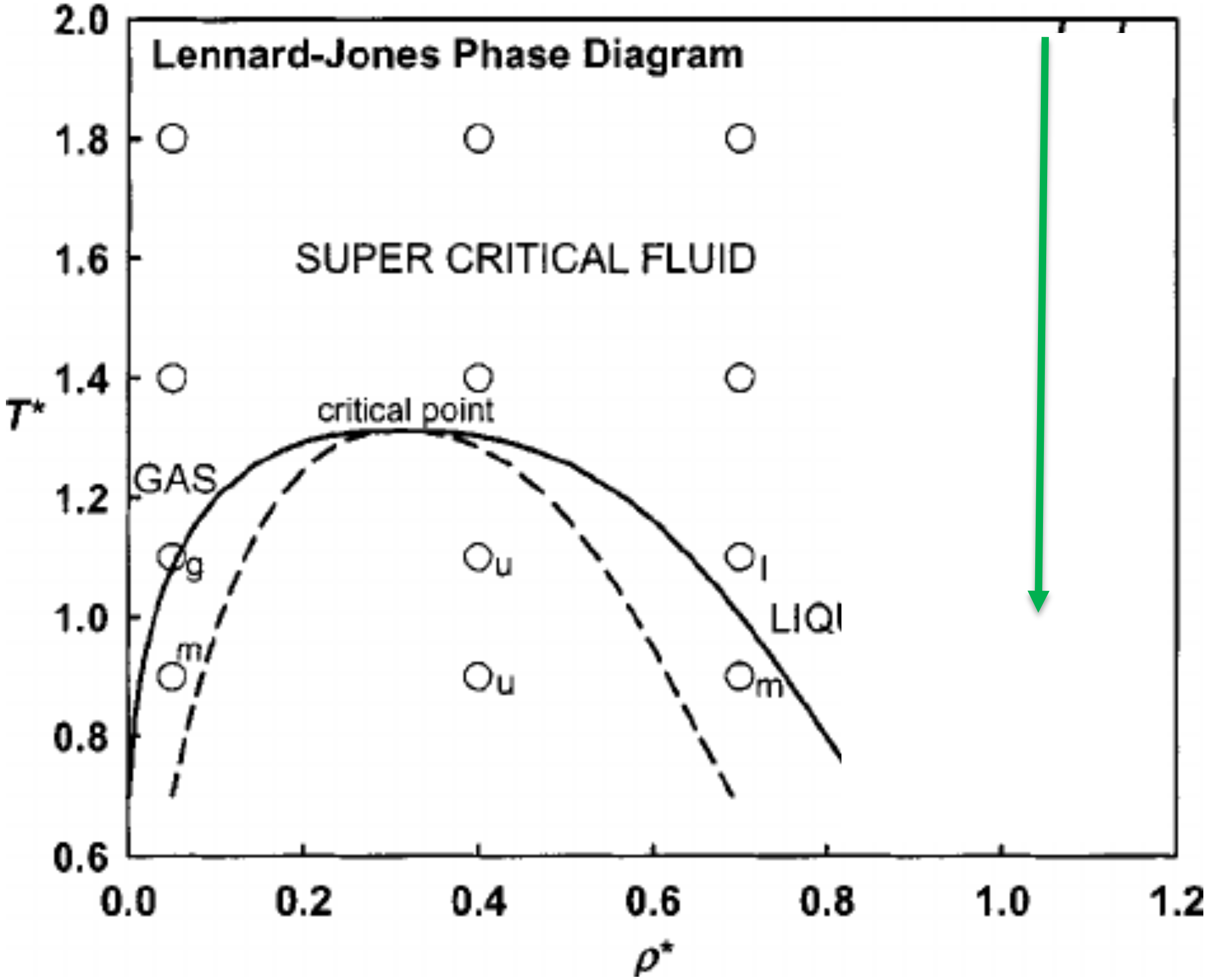
Quenching a dense liquid:



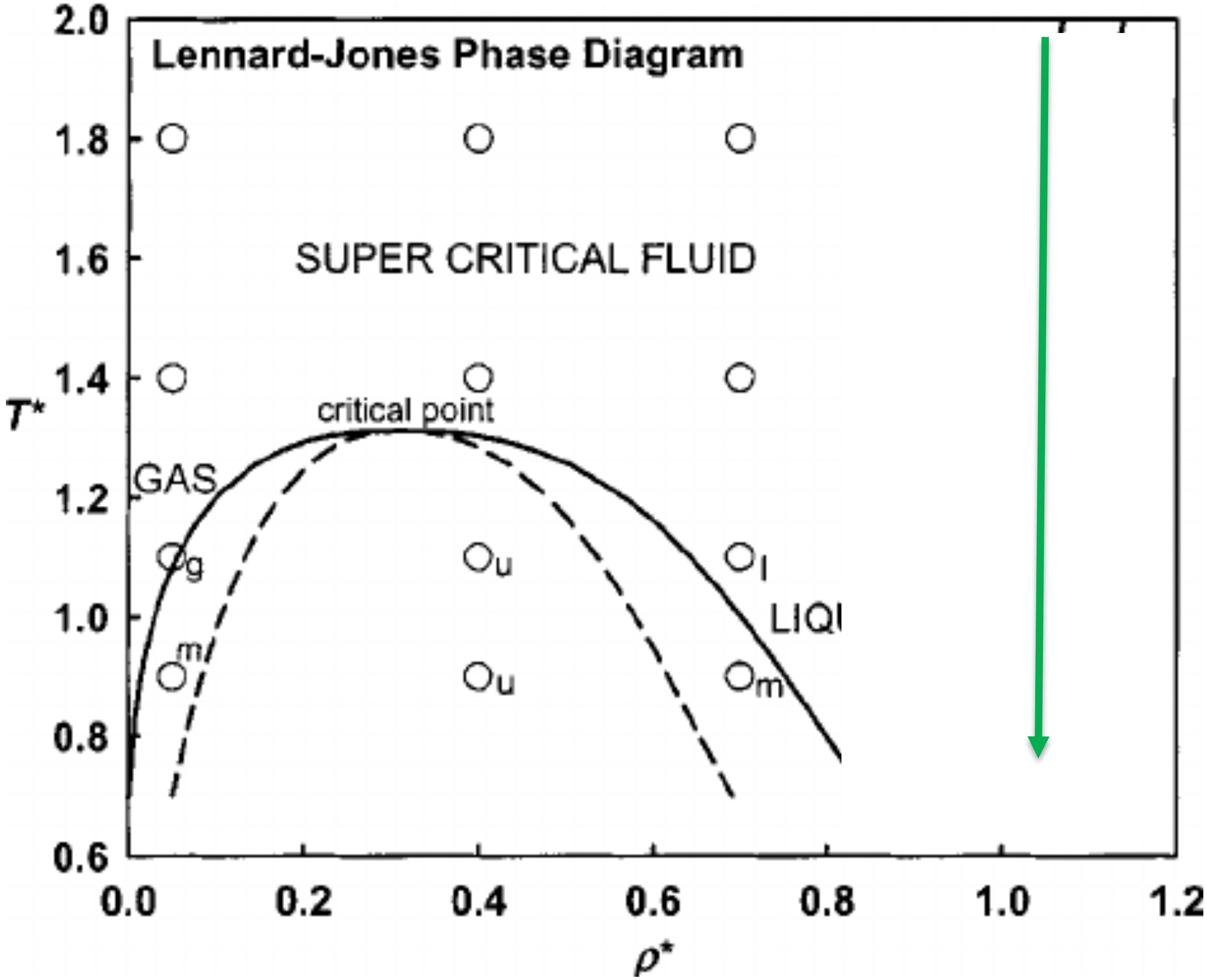
Quenching a dense liquid:



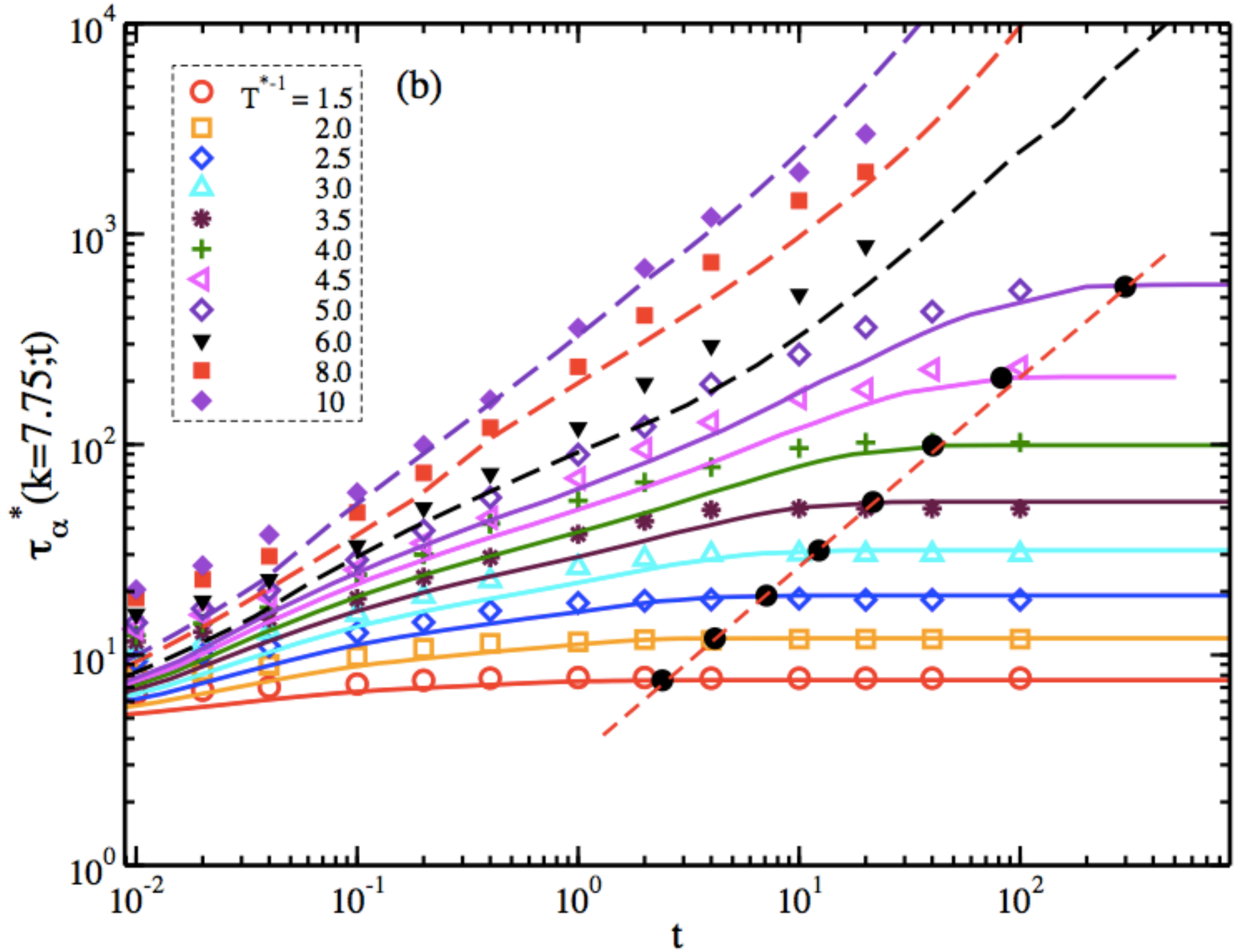
Quenching a dense liquid:



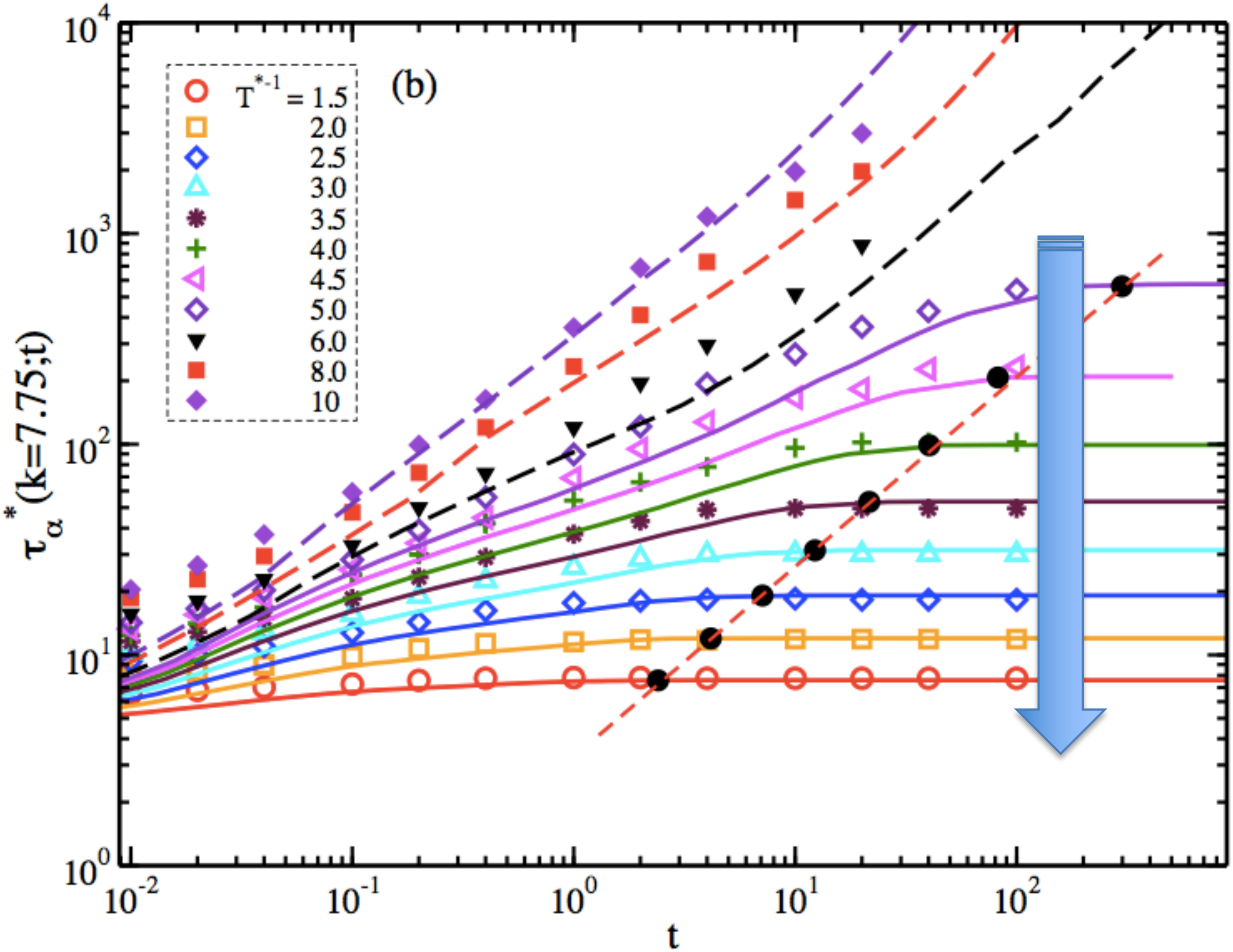
Quenching a dense liquid:



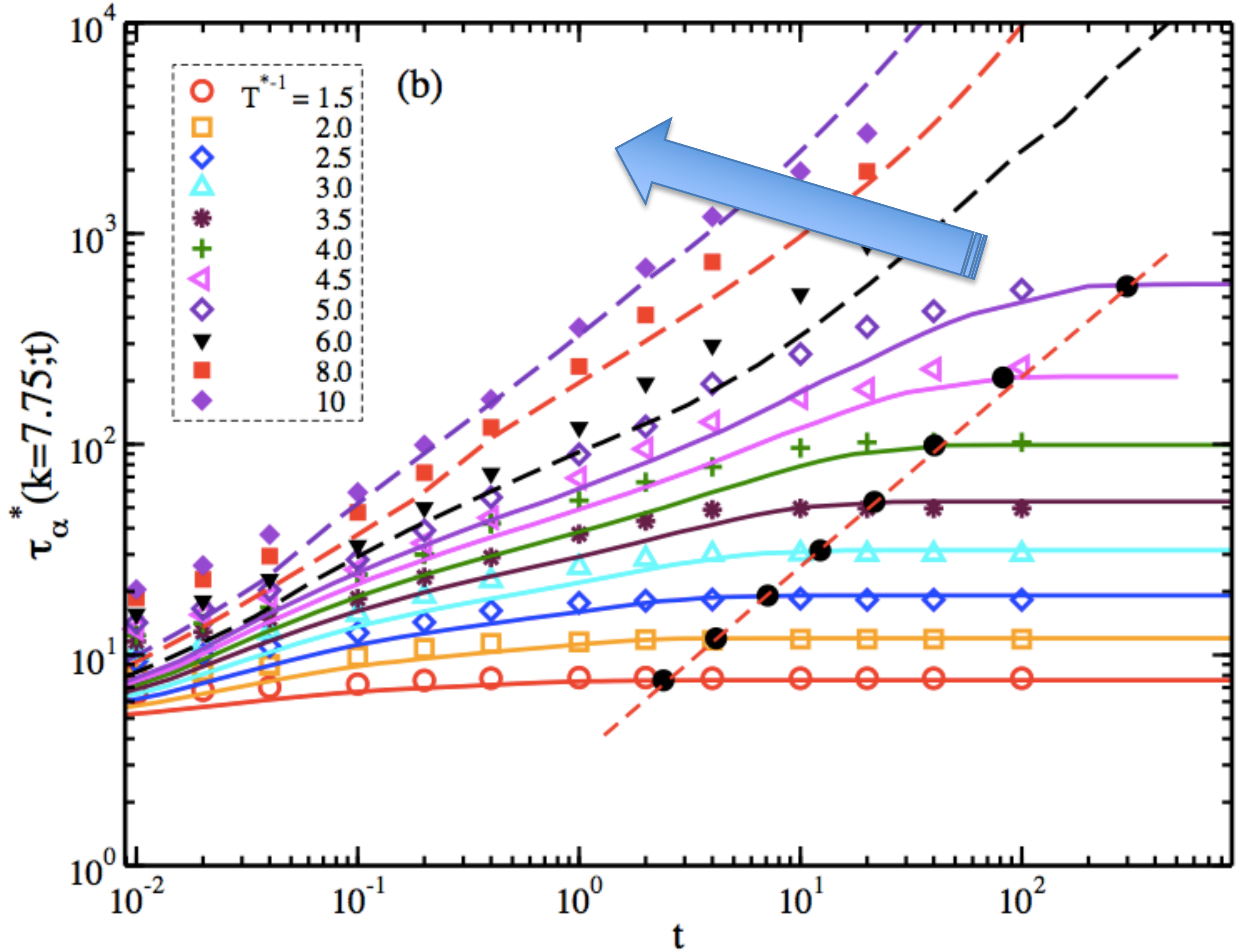
Tiempo de relajación (o viscosidad)



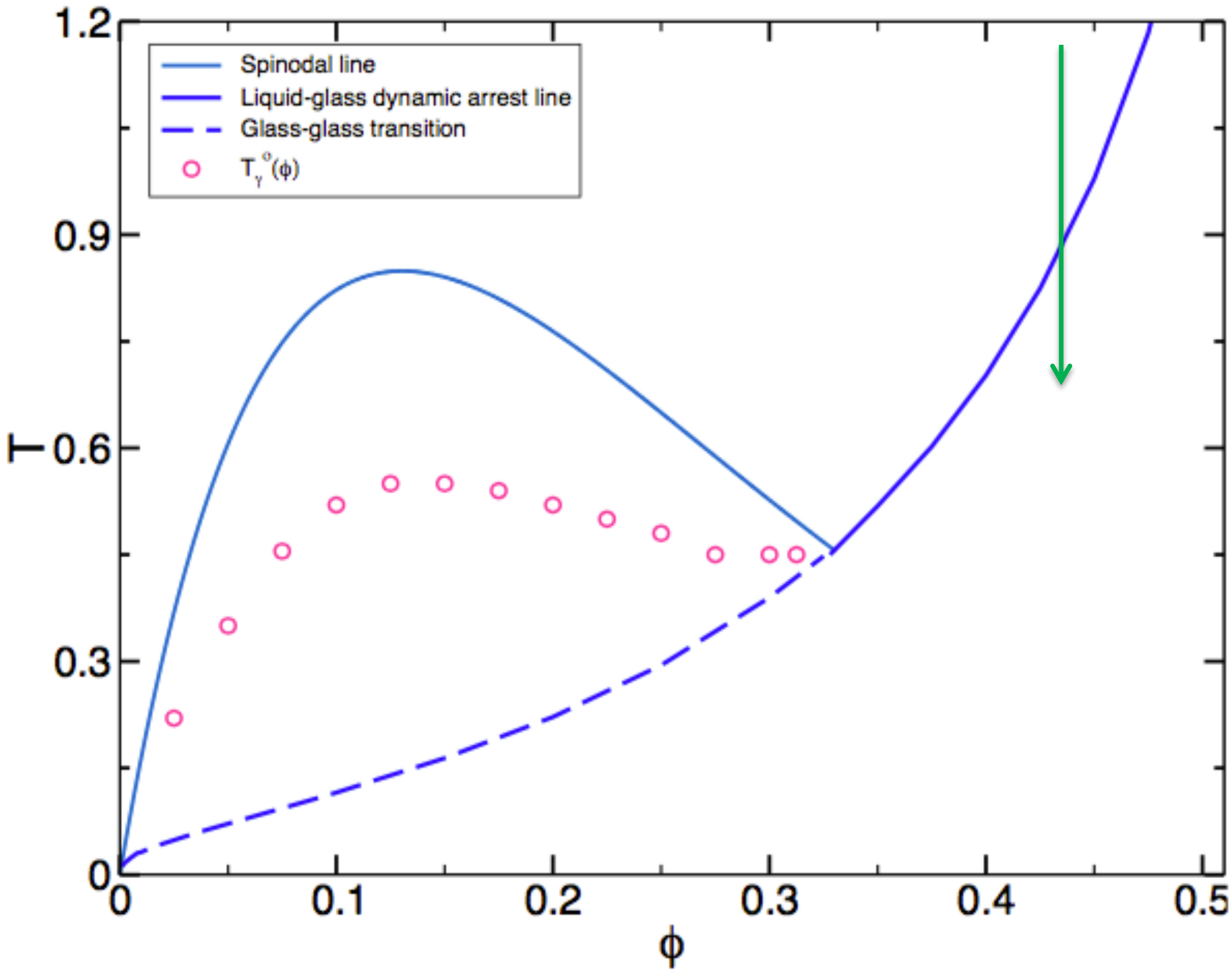
Two regimes: Equilibration



Two regimes: Aging



PREDICTED SCENARIO:



THE JOURNAL OF CHEMICAL PHYSICS **143**, 174505 (2015)

Non-equilibrium theory of arrested spinodal decomposition

José Manuel Olais-Govea, Leticia López-Flores, and Magdaleno Medina-Noyola
Instituto de Física "Manuel Sandoval Vallarta," Universidad Autónoma de San Luis Potosí,
Álvaro Obregón 64, 78000 San Luis Potosí, SLP, Mexico

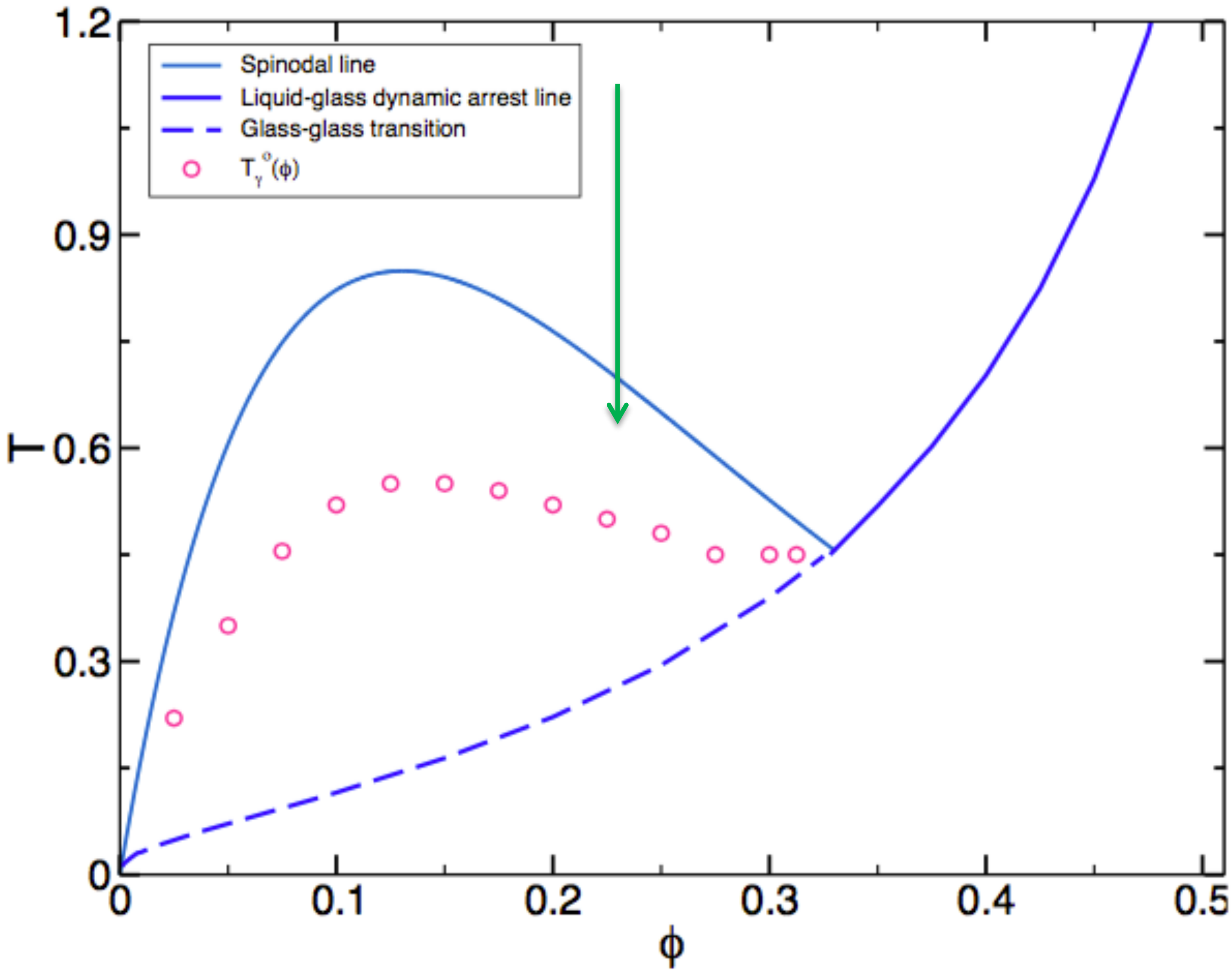
(Received 3 May 2015; accepted 19 October 2015; published online 6 November 2015)

Non-equilibrium Kinetics of the Transformation of Liquids into Physical Gels

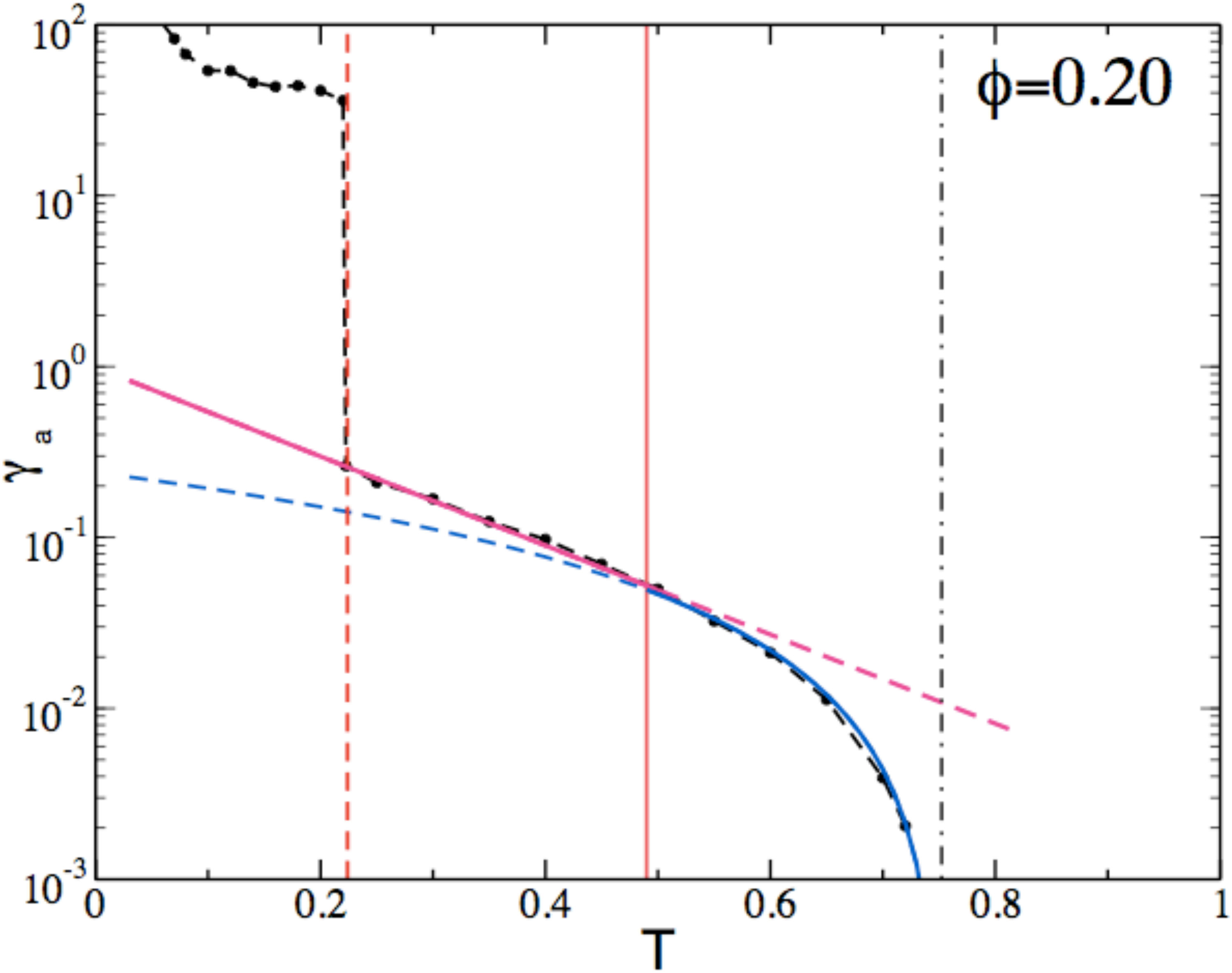
José Manuel Olais-Govea, Leticia López-Flores*, Martín Chávez-Páez, and Magdaleno Medina-Noyola
Instituto de Física "Manuel Sandoval Vallarta", Universidad Autónoma de San Luis Potosí,
Álvaro Obregón 64, 78000 San Luis Potosí, SLP, México

(Dated: May 3, 2018)

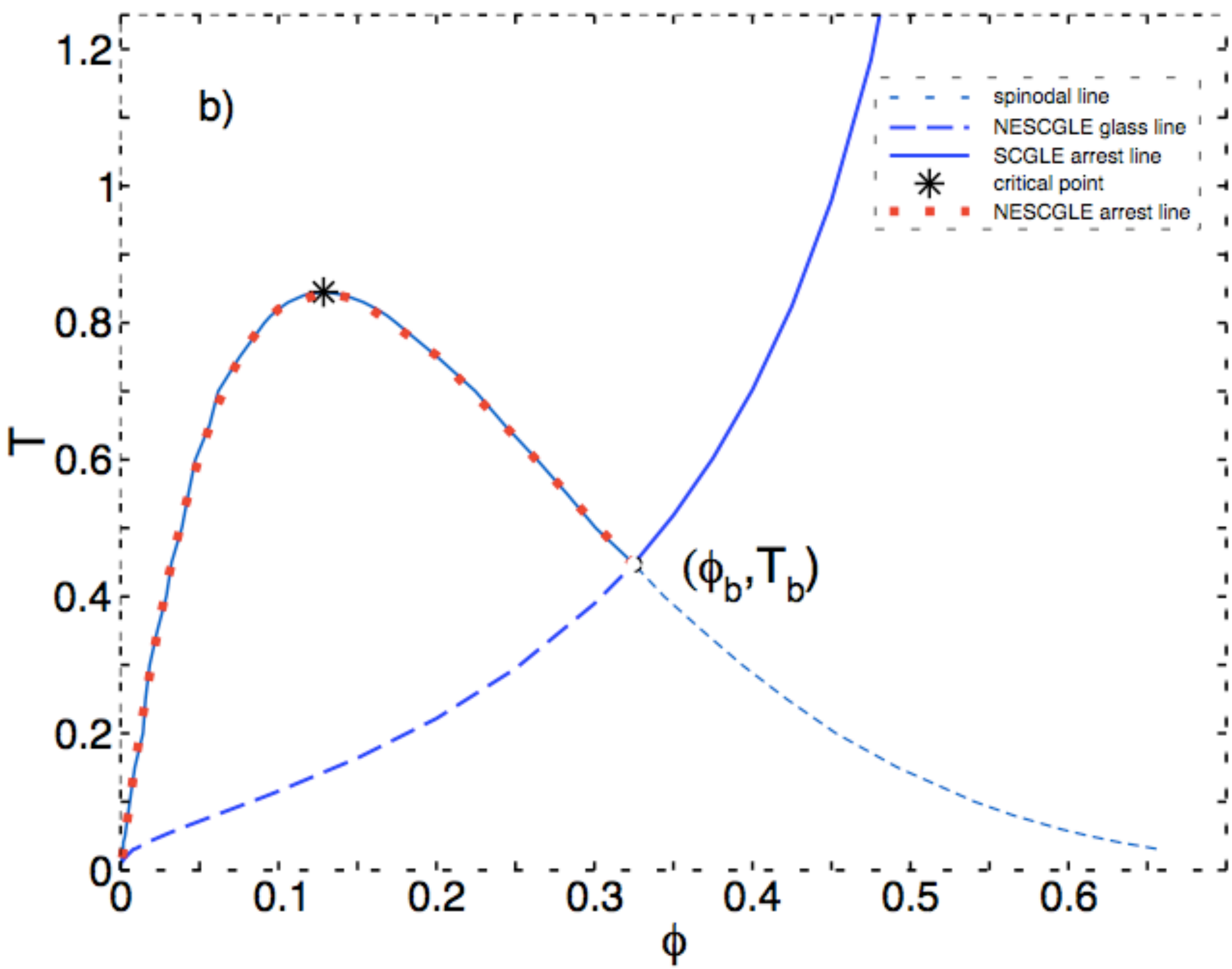
PREDICTED SCENARIO:



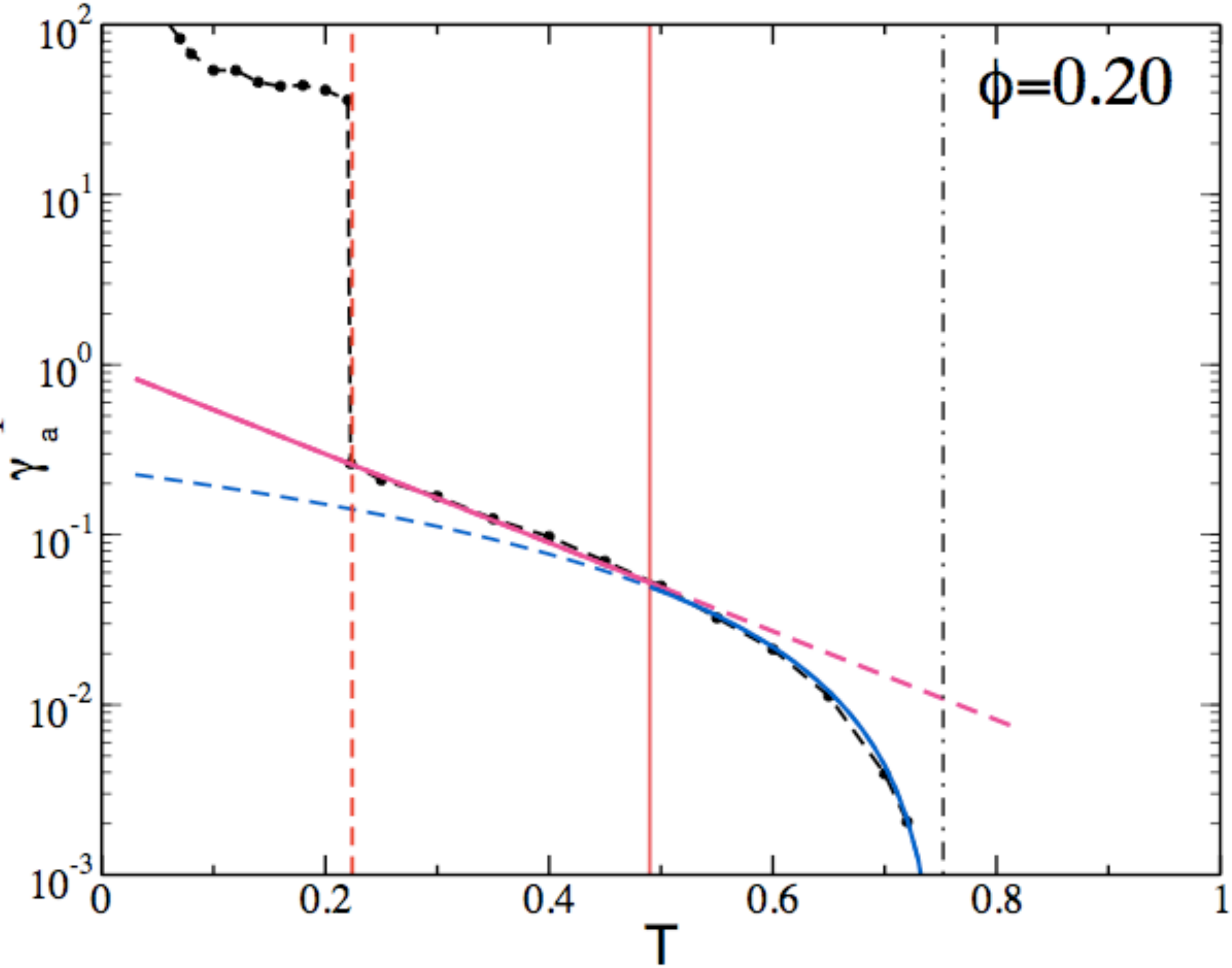
ESCENARIO PREDICHO (NE-SCGLE)



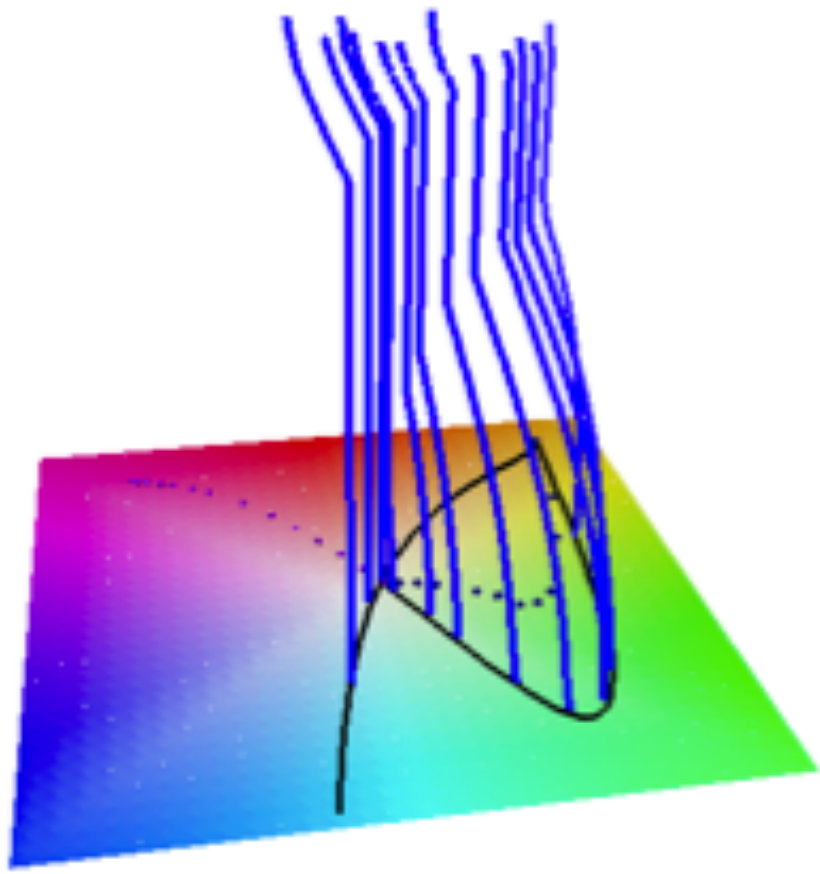
ESCENARIO PREDICHO (NE-SCGLE)



ESCENARIO PREDICHO (NE-SCGLE)

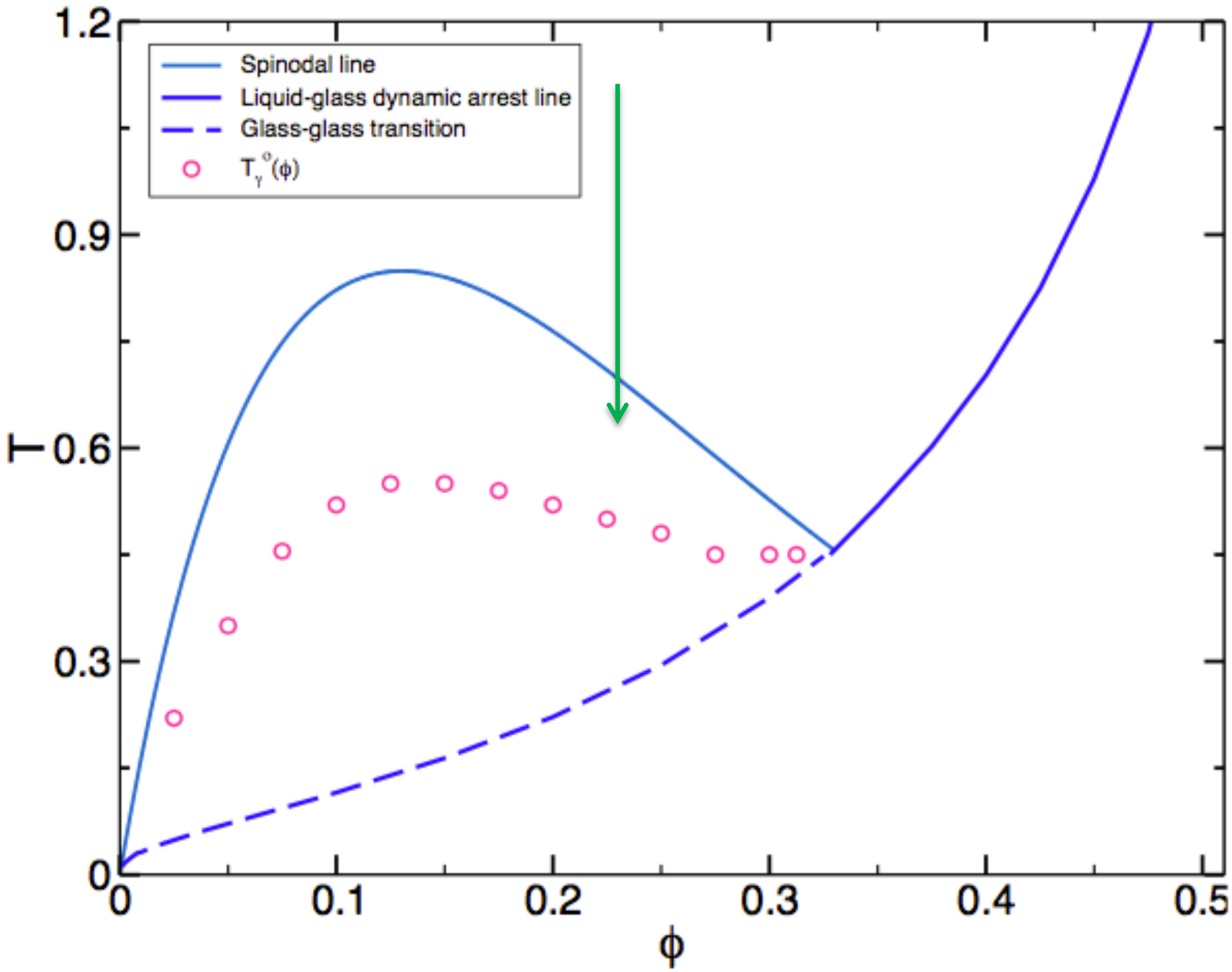


ESCENARIO PREDICHO (NE-SCGLE)



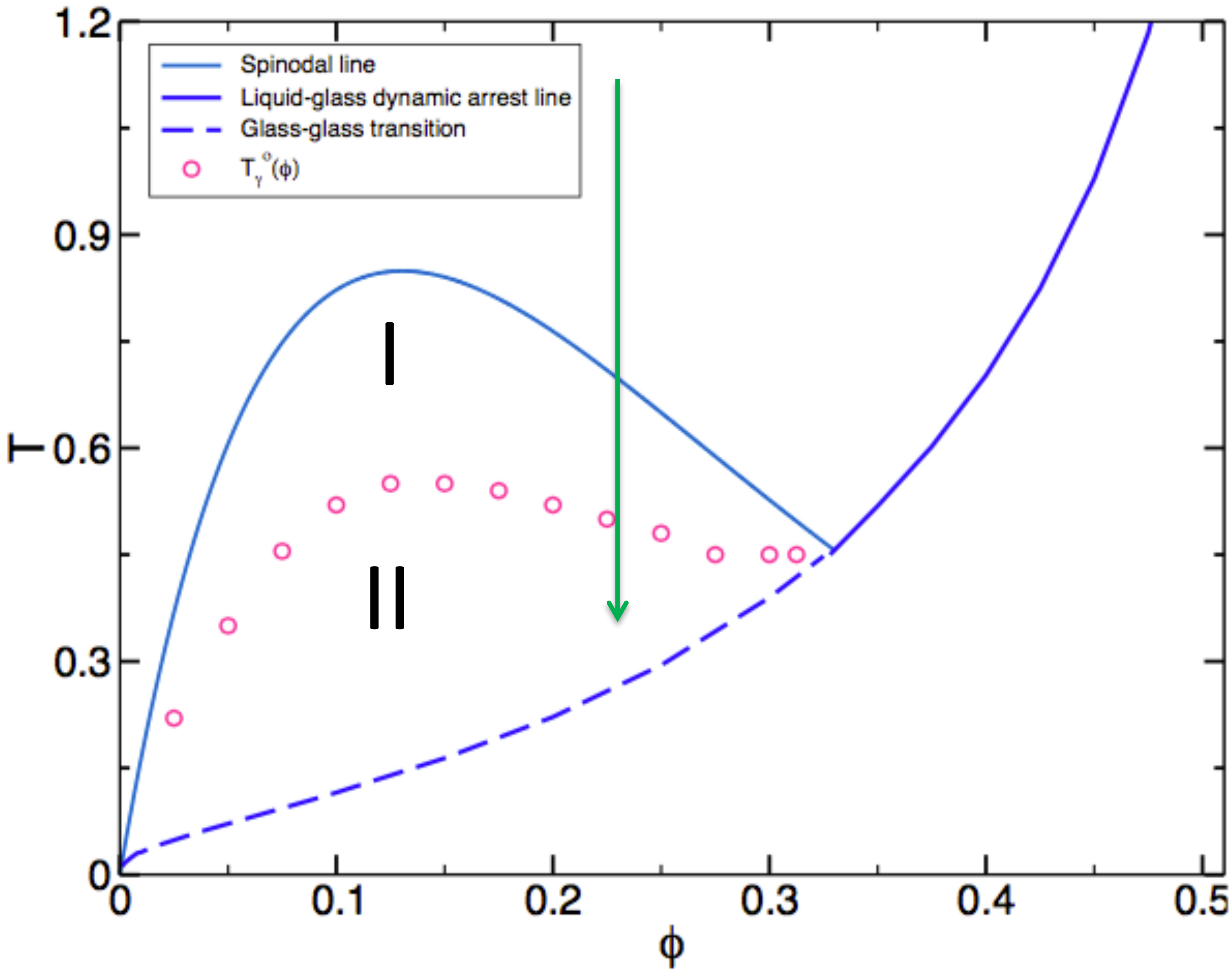
ESCENARIO PREDICHO (NE-SCGLE)

PREDICTED SCENARIO:

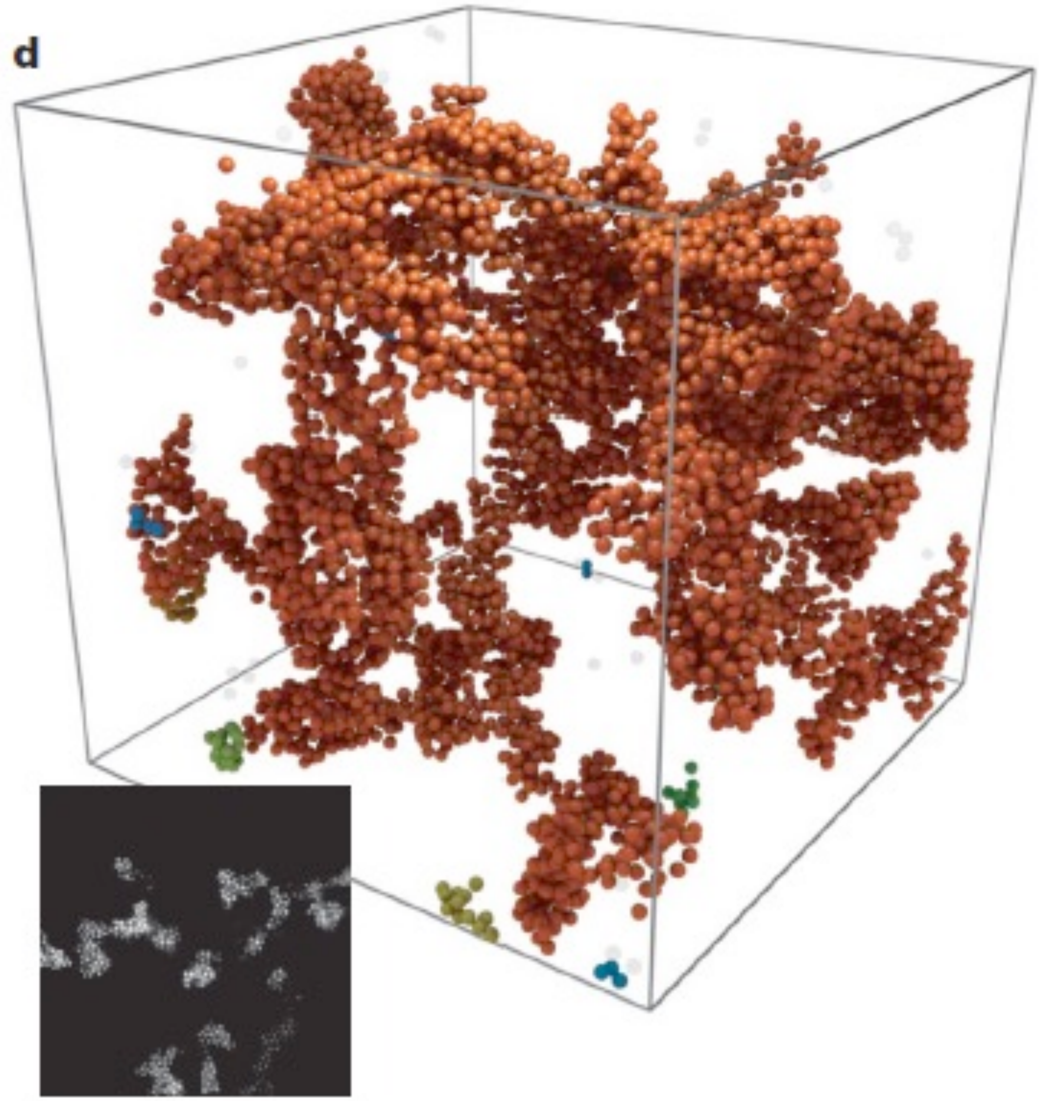


Separación Gas-Líquido:

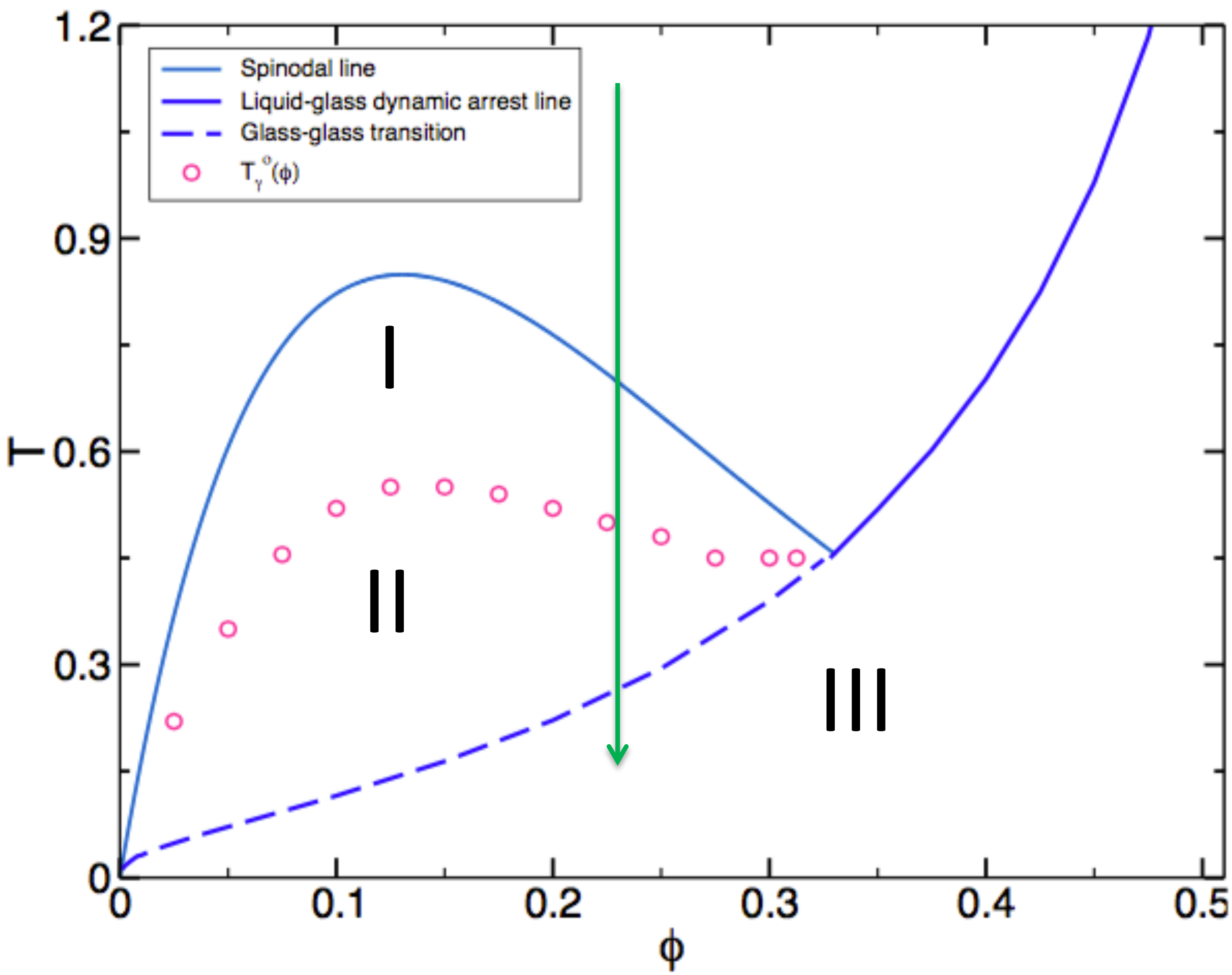
ESCENARIO PREDICHO:



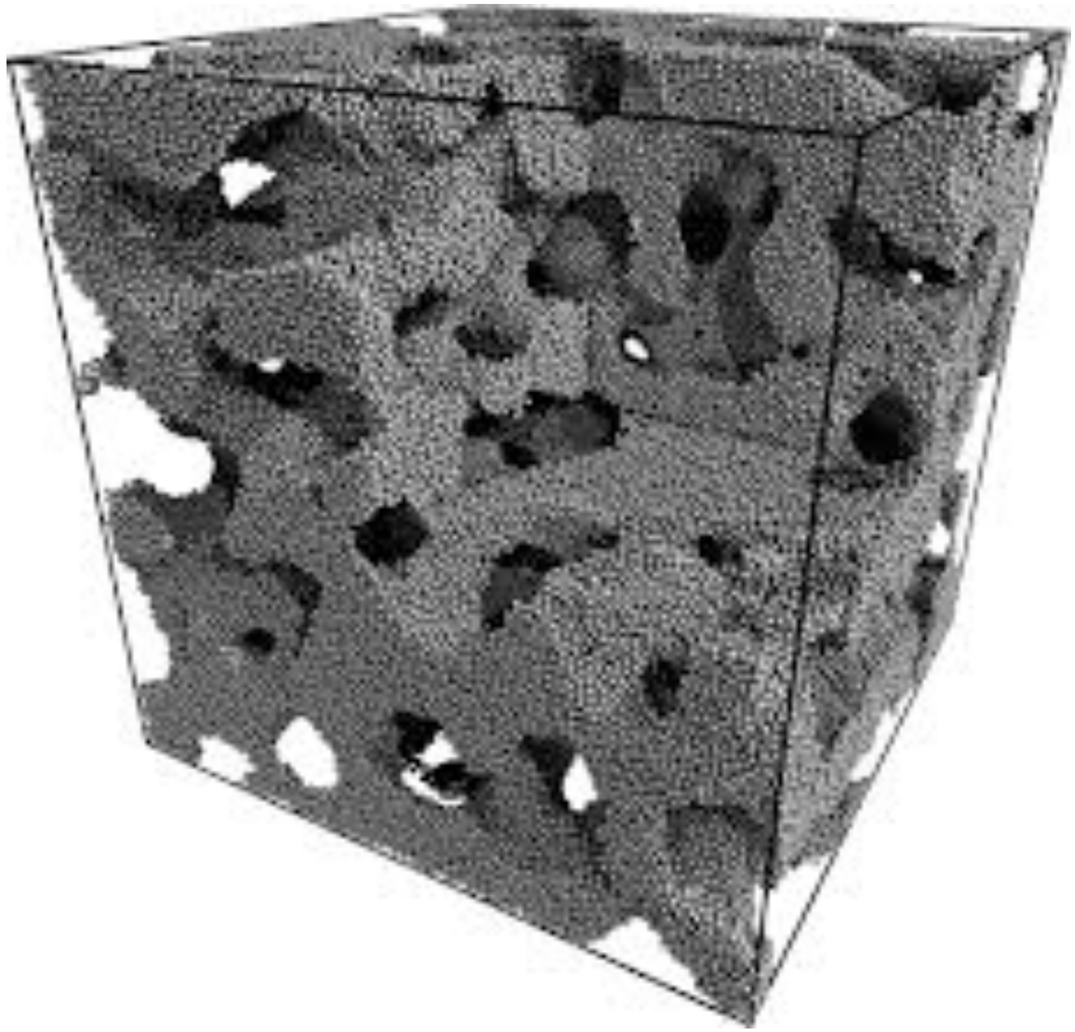
GELS



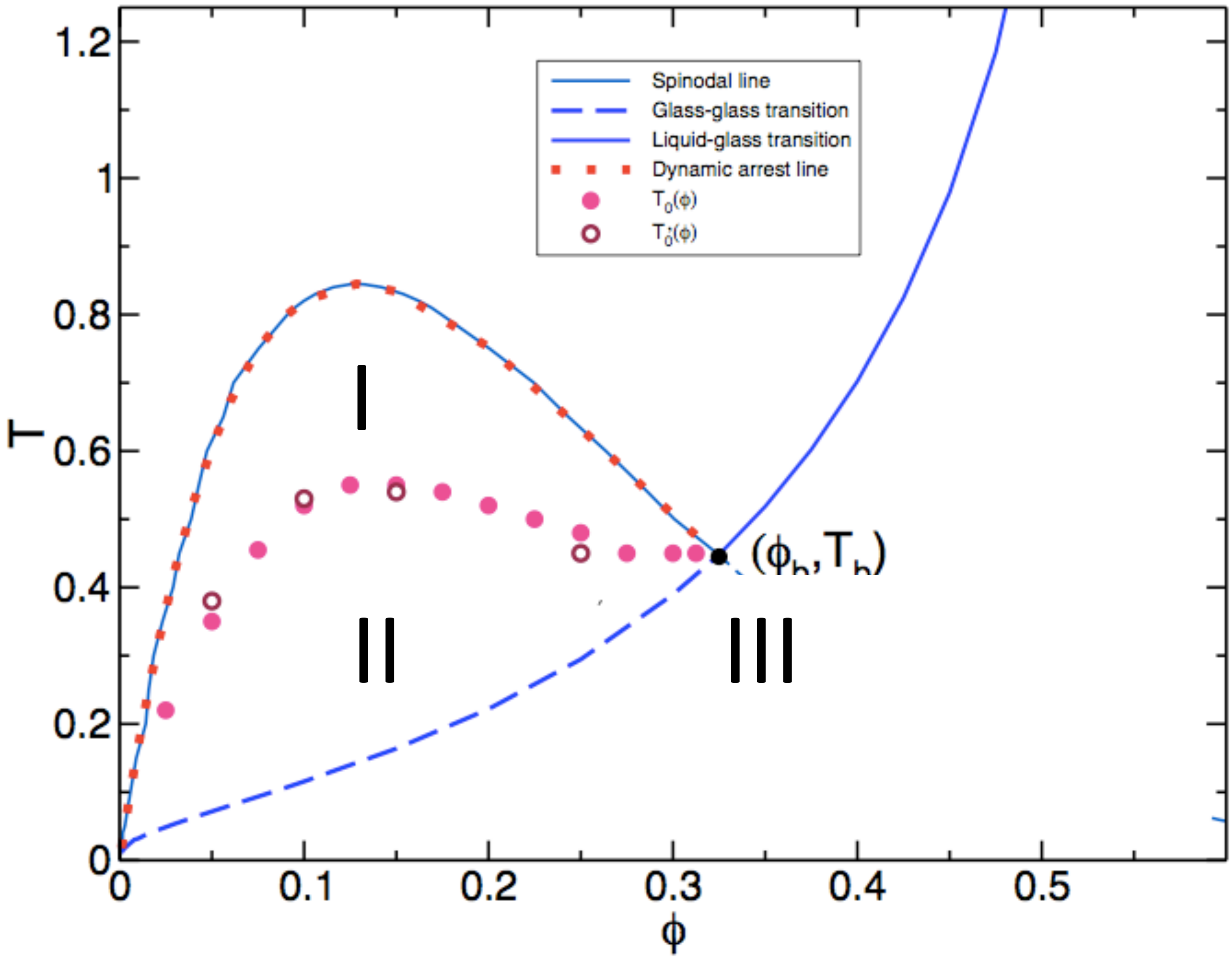
ESCENARIO PREDICHO:



POROUS GLASSES



ESCENARIO PREDICHO (NE-SCGLE)



OBSERVED SCENARIO :

Cite this: *Soft Matter*, 2011, **7**, 857

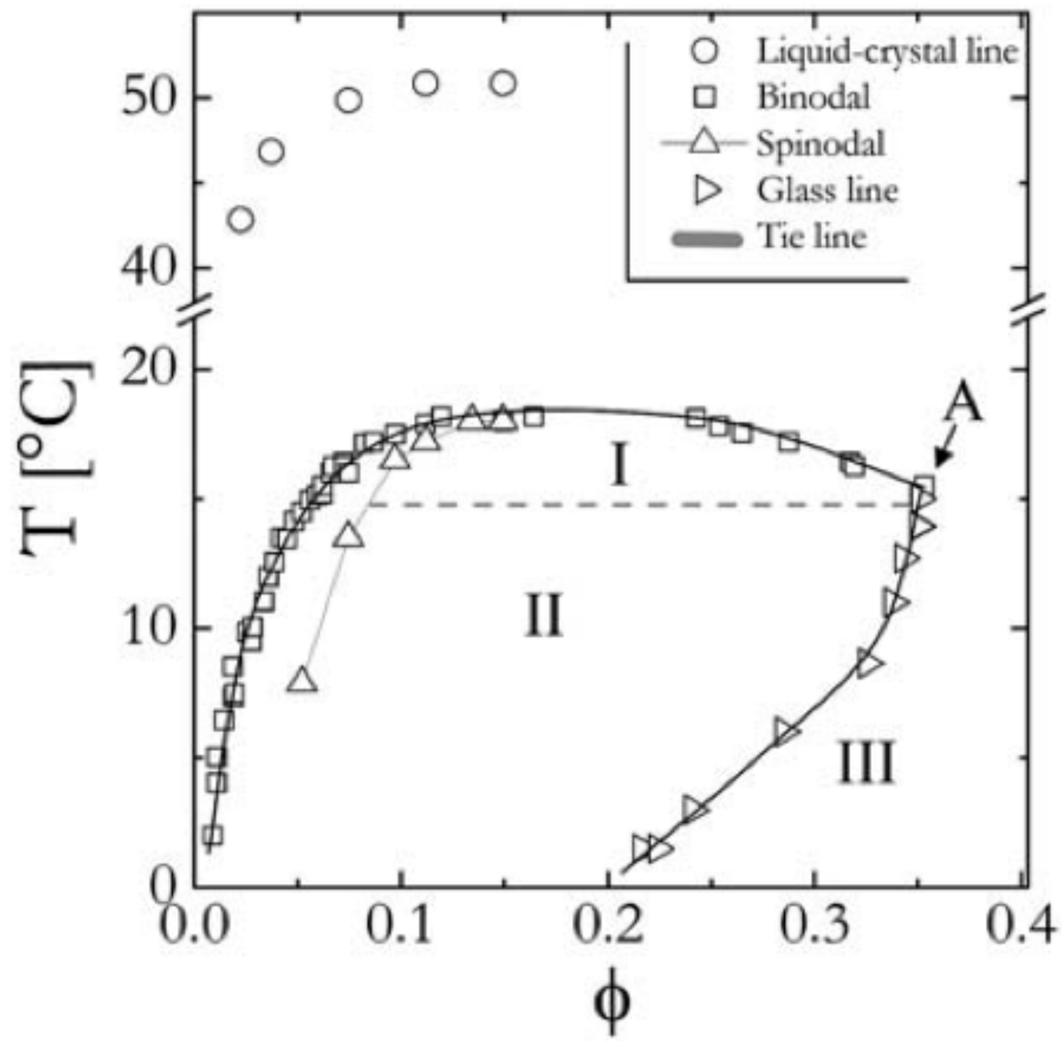
www.softmatter.org

COMMUNICATION

Phase separation and dynamical arrest for particles interacting with mixed potentials—the case of globular proteins revisited†

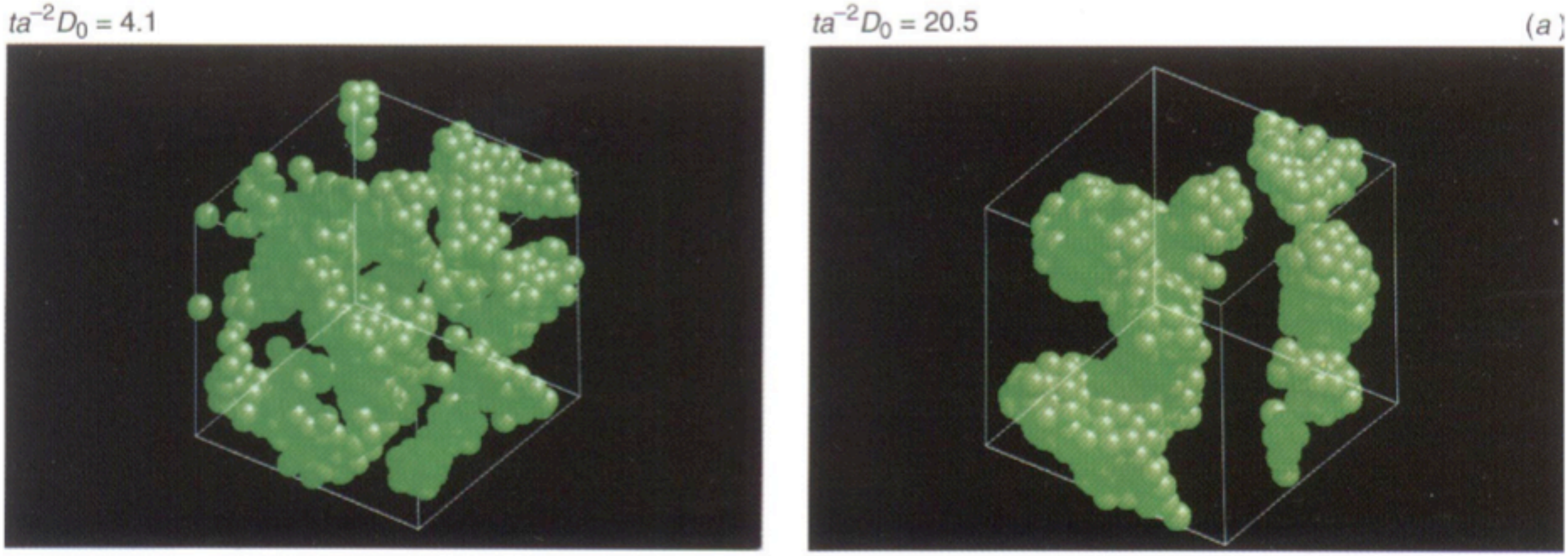
Thomas Gibaud,‡[a] Frédéric Cardinaux,[a] Johan Bergenholtz,[b] Anna Stradner[c] and Peter Schurtenberger*[d]

OBSERVED SCENARIO :



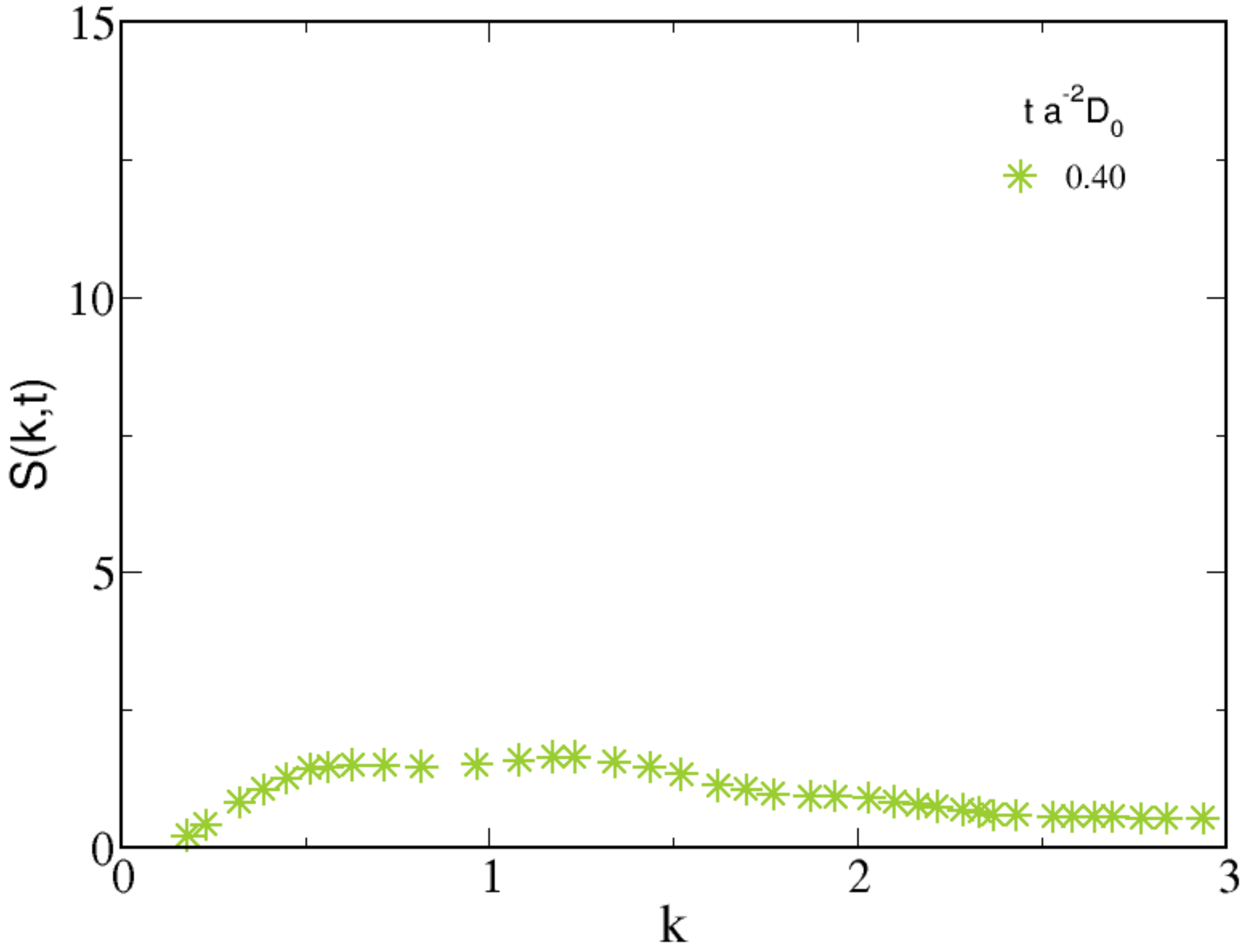
AND HOW ABOUT KINETICS?

Separación Gas-Líquido en el Fluido de Lennard-Jones

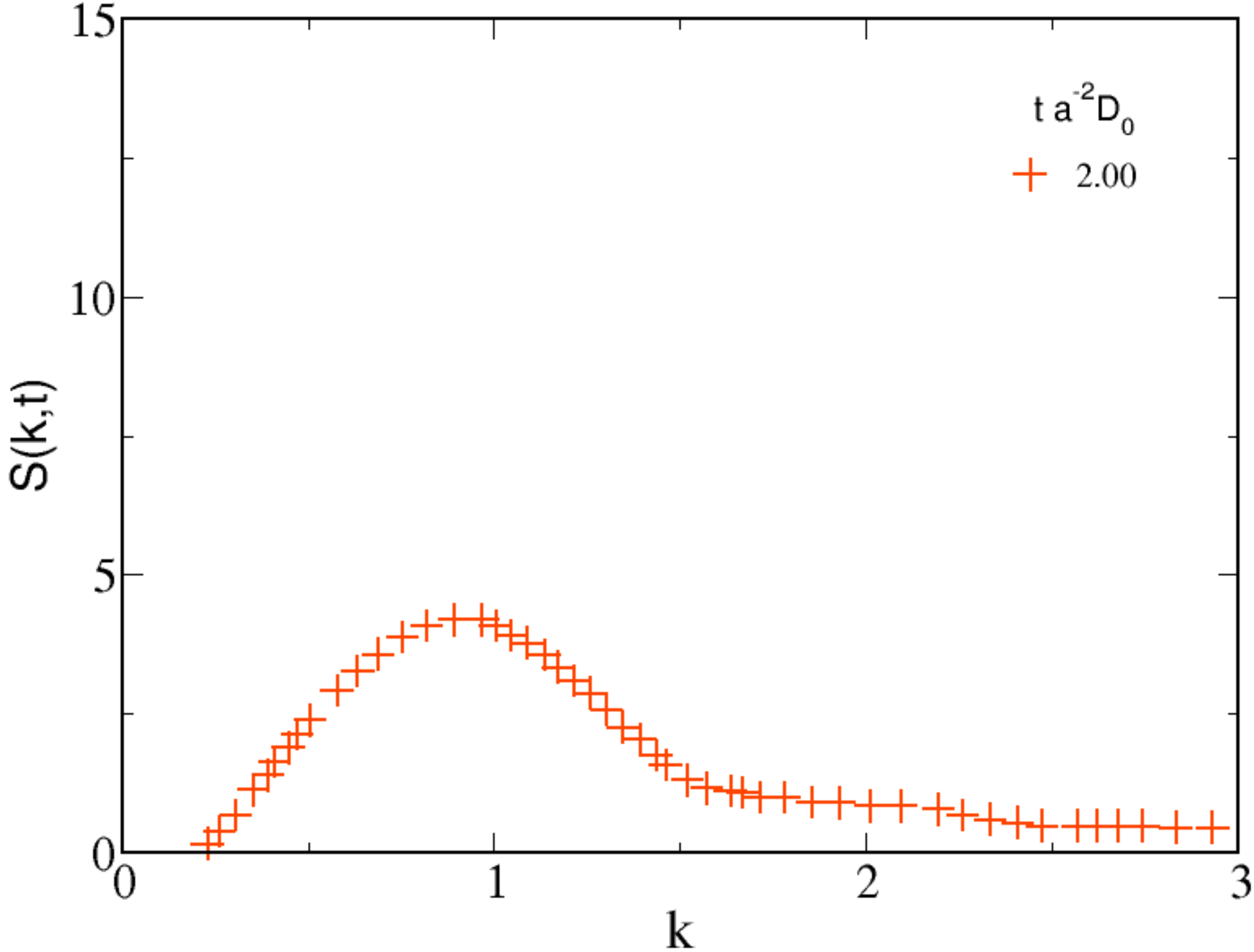


J. Felicity M. Lodge and David M. Heyes

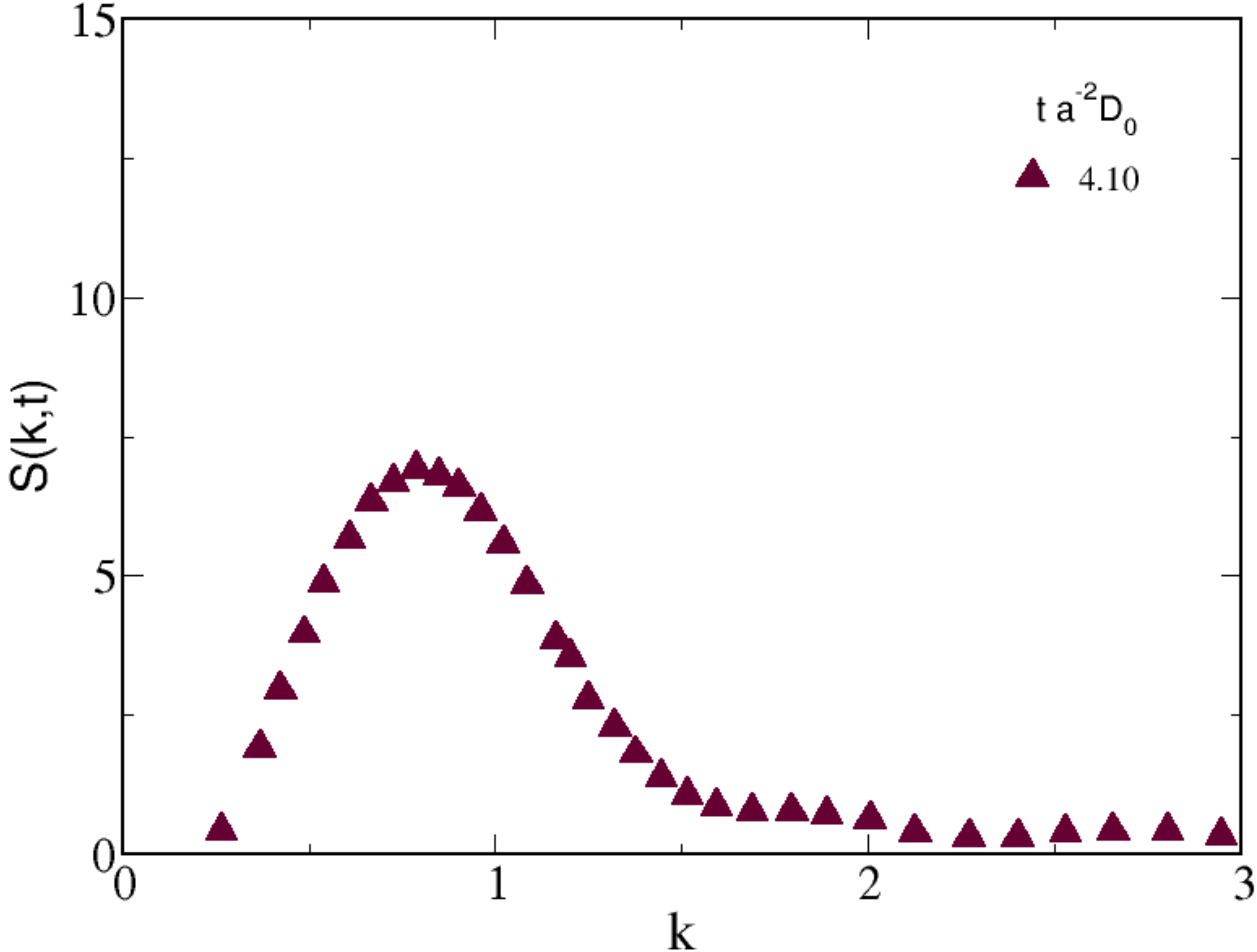
J. Chem. Soc., Faraday Trans., 1997, **93**(3), 437



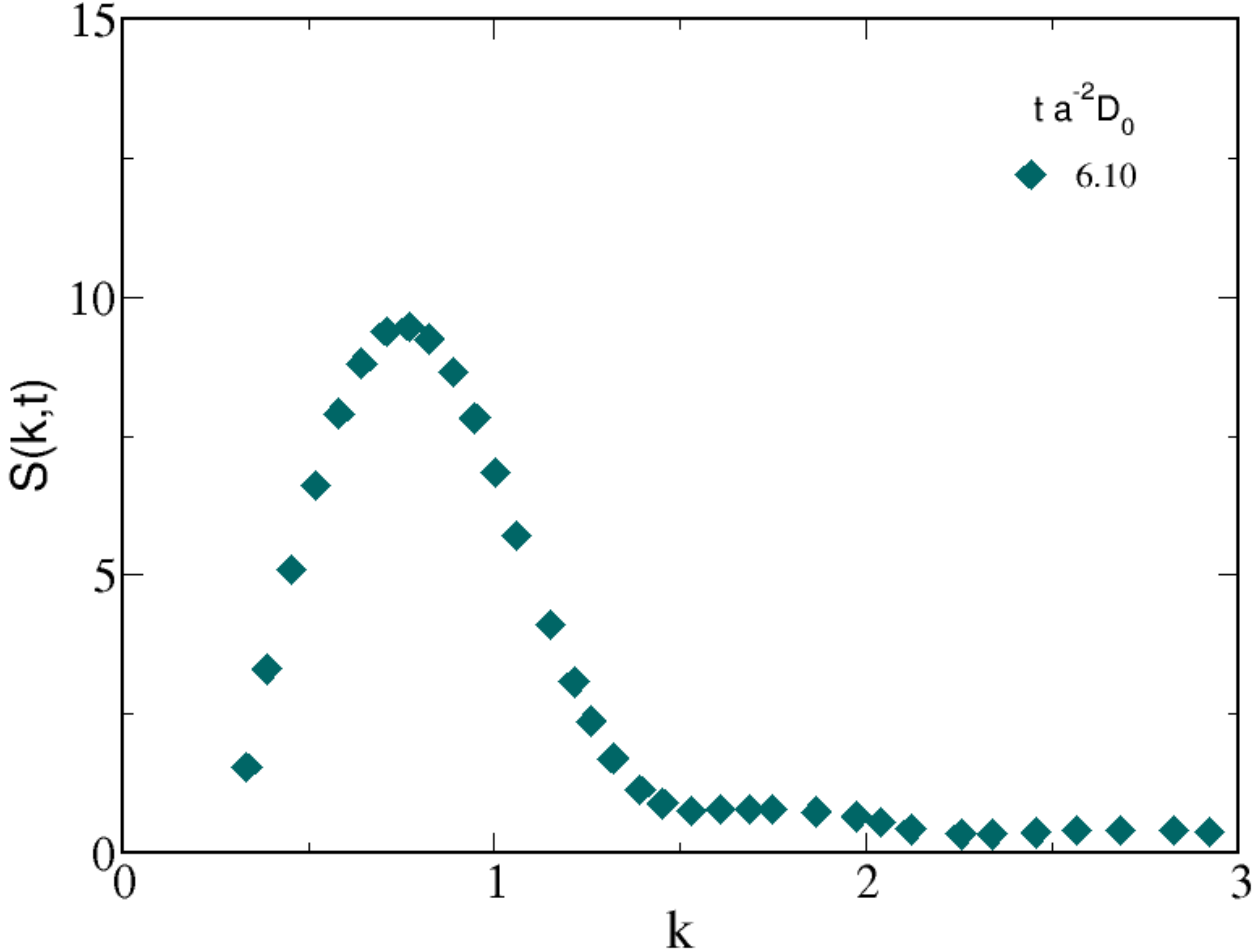
15
10
5
0
S(k,t)
0
1
2
3
k
$t\ a^{-2}D_0$
0.40



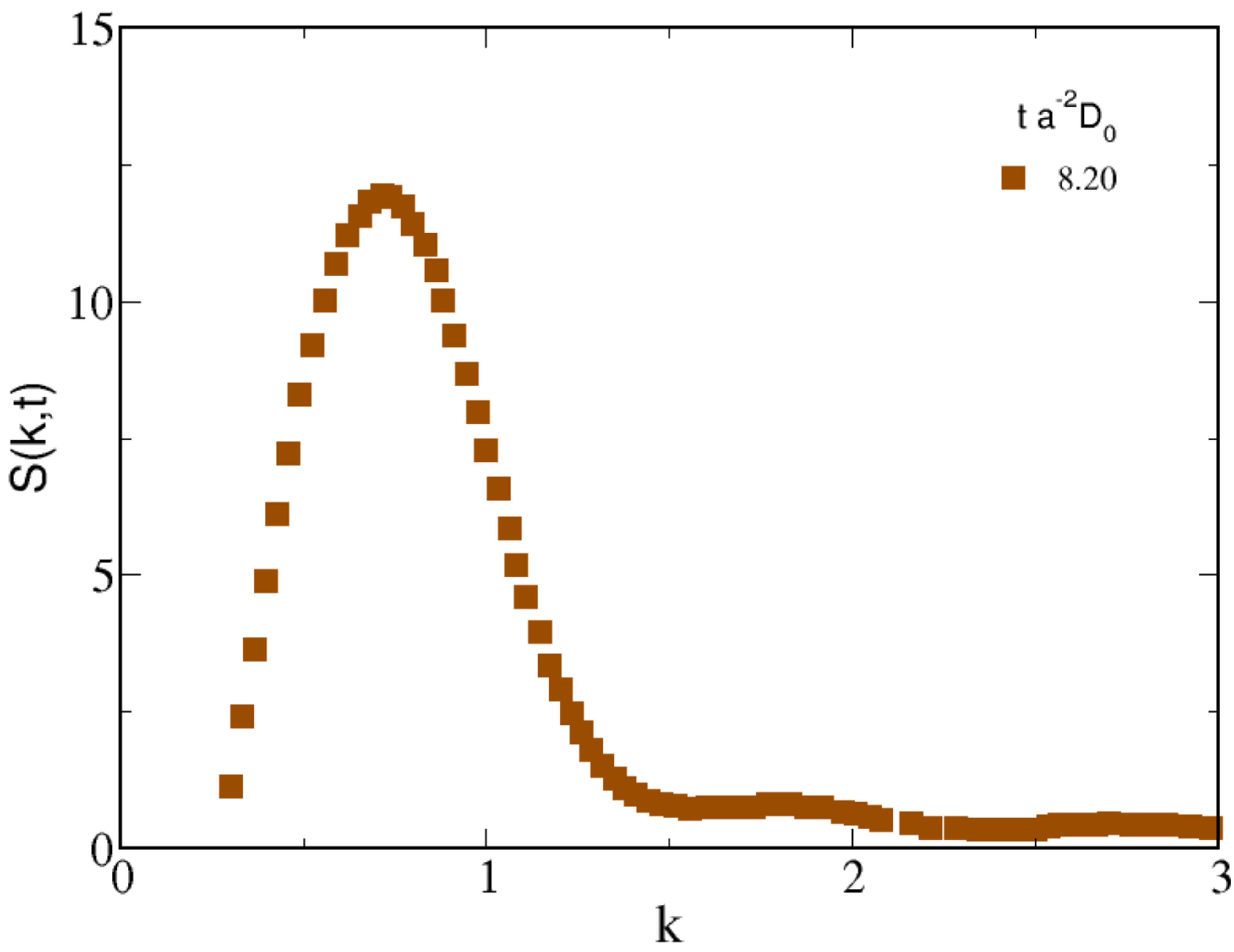
t a^-2 D_0
2.00
15
10
5
0
S(k,t)
0
1
2
3
k

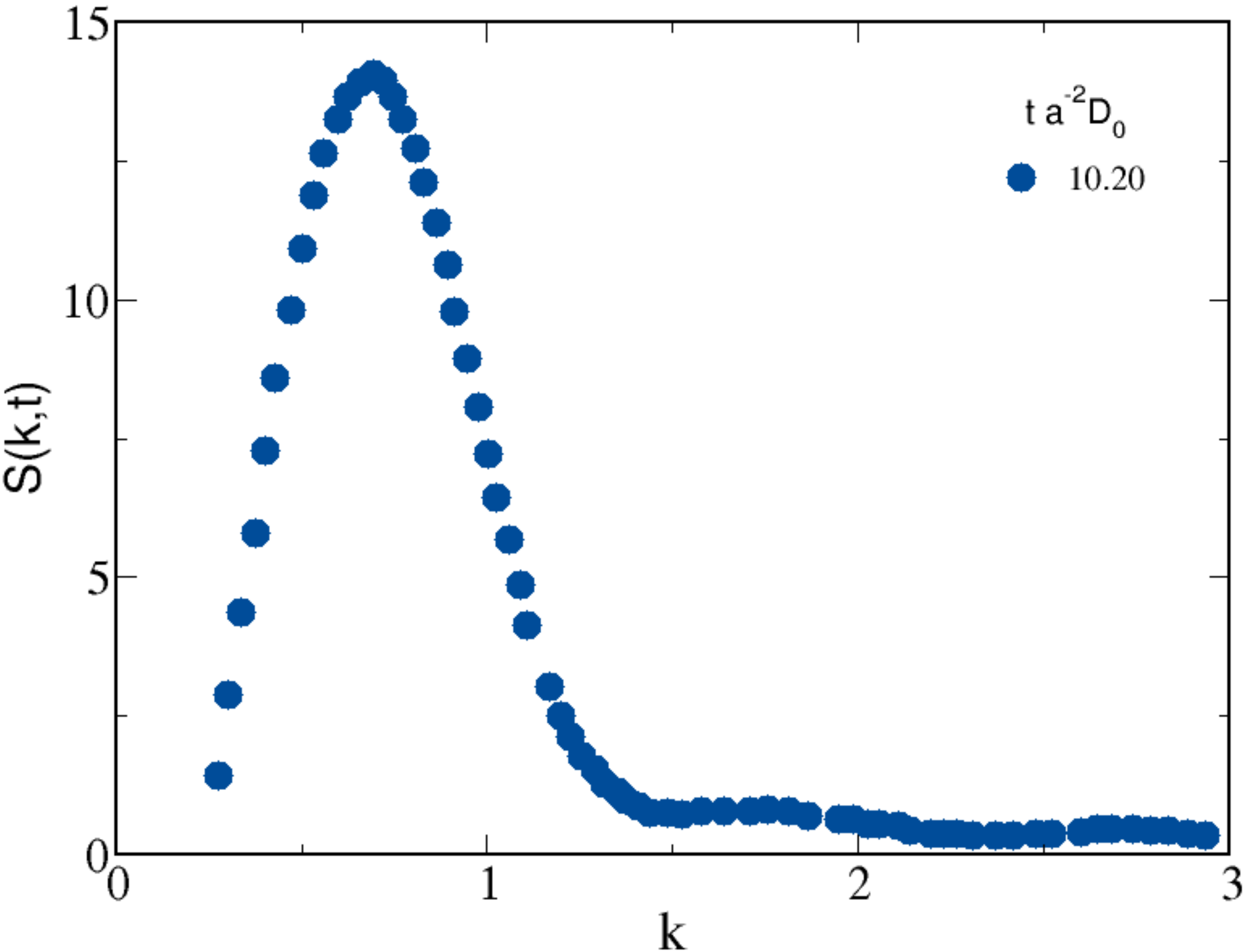


t a^{-2}D$_0$
4.10
S(k,t)
k
0
5
10
15
0
1
2
3



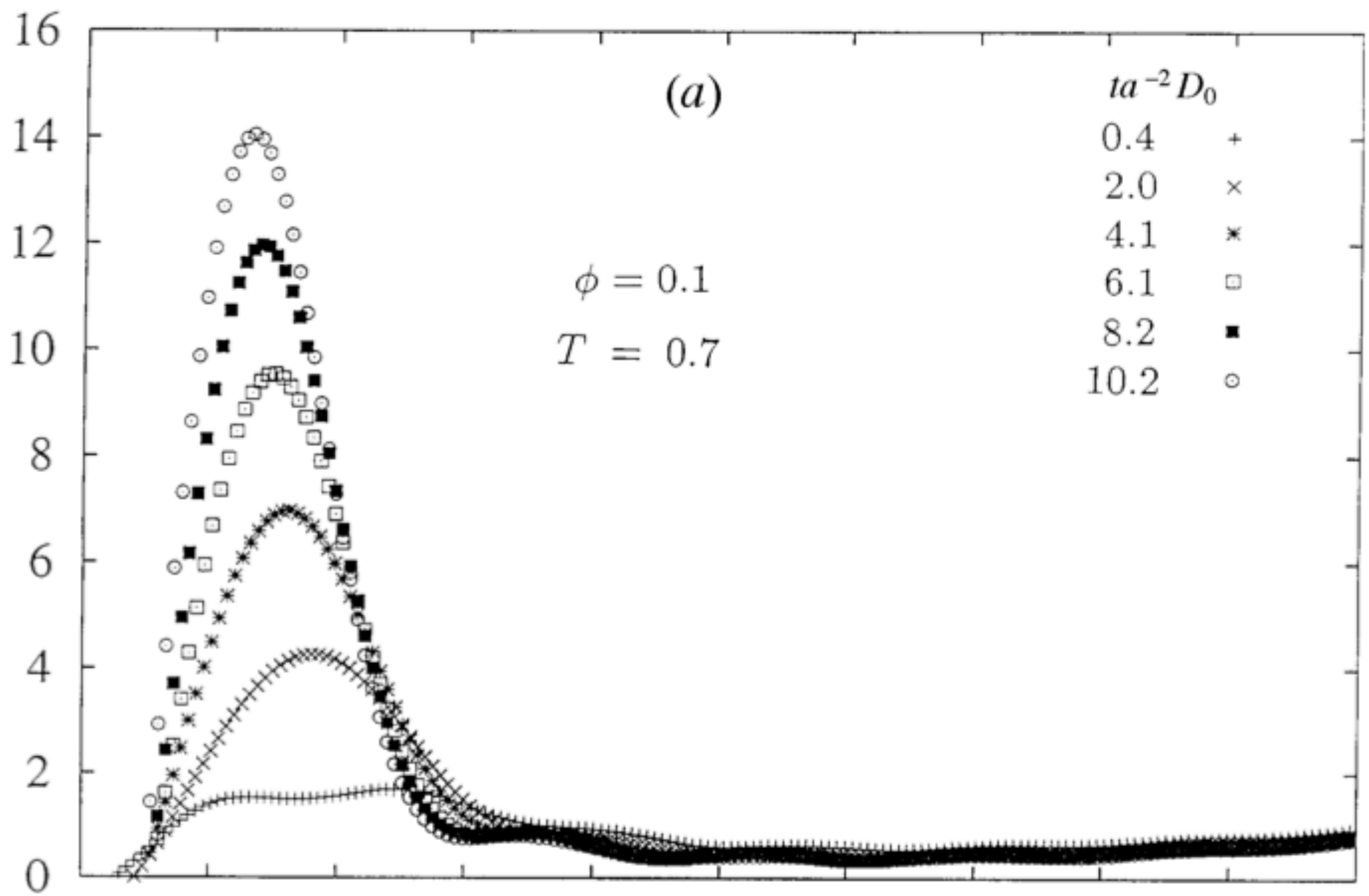
15
10
5
0
0
1
2
3
k
S(k,t)
t a^-2 D_0
6.10


15
10
5
0
0
1
2
3
k
S(k,t)
t a^-2 D_0
8.20



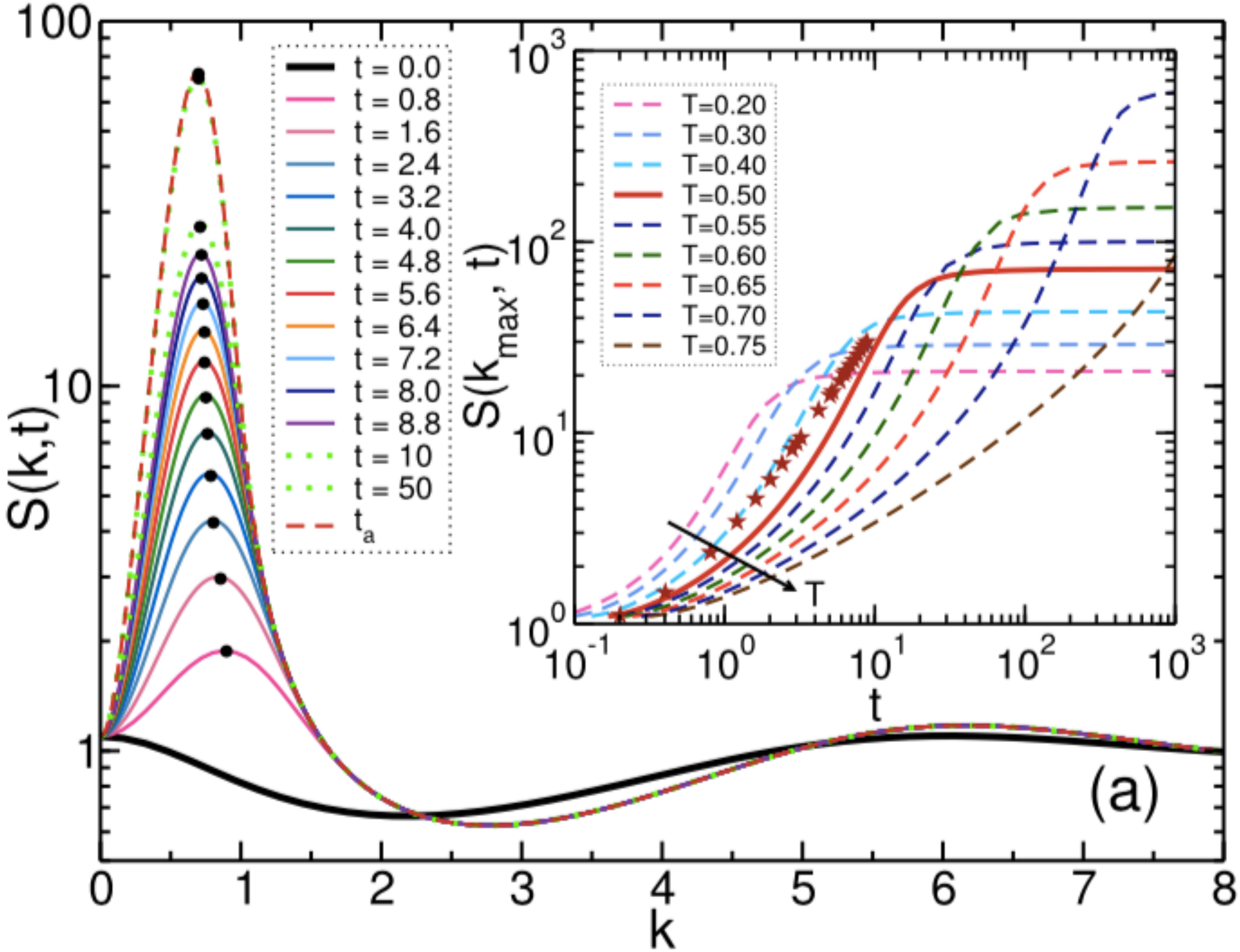
S(k,t)
k
15
10
5
0
0
1
2
3
t a^-2 D_0
10.20

Separación Gas-Líquido en el Fluido de Lennard-Jones

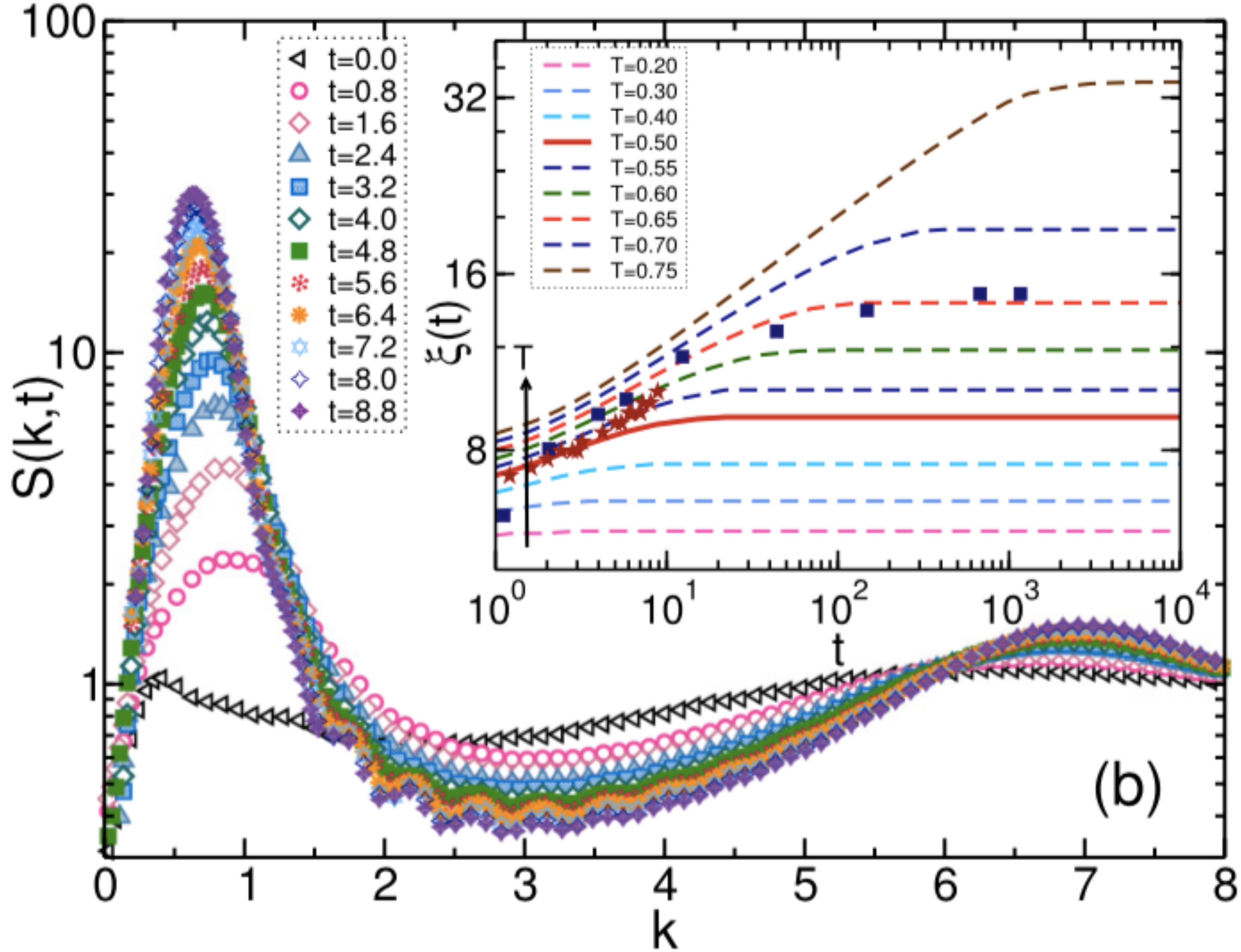


J. Felicity M. Lodge and David M. Heyes

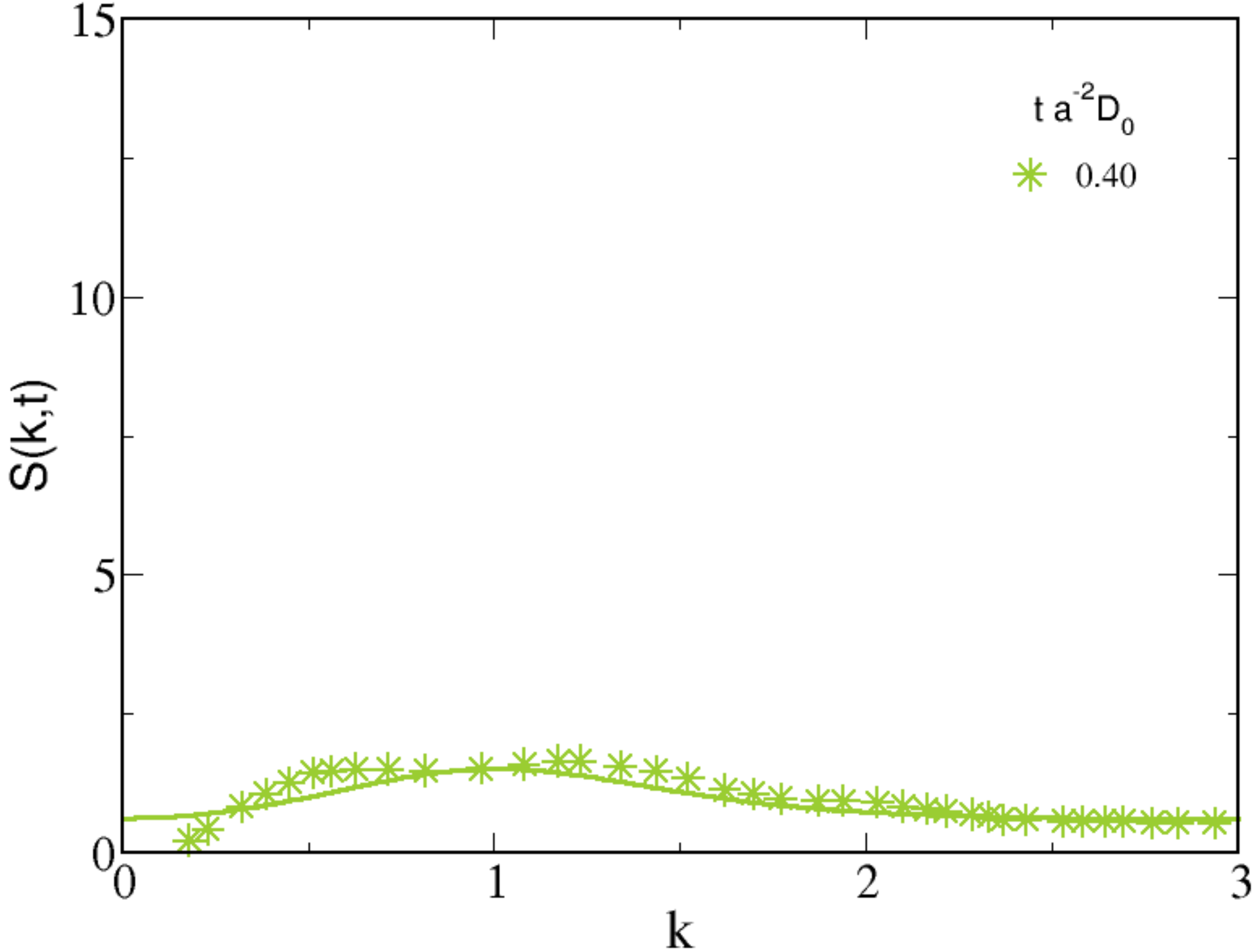
J. Chem. Soc., Faraday Trans., 1997, **93**(3), 437



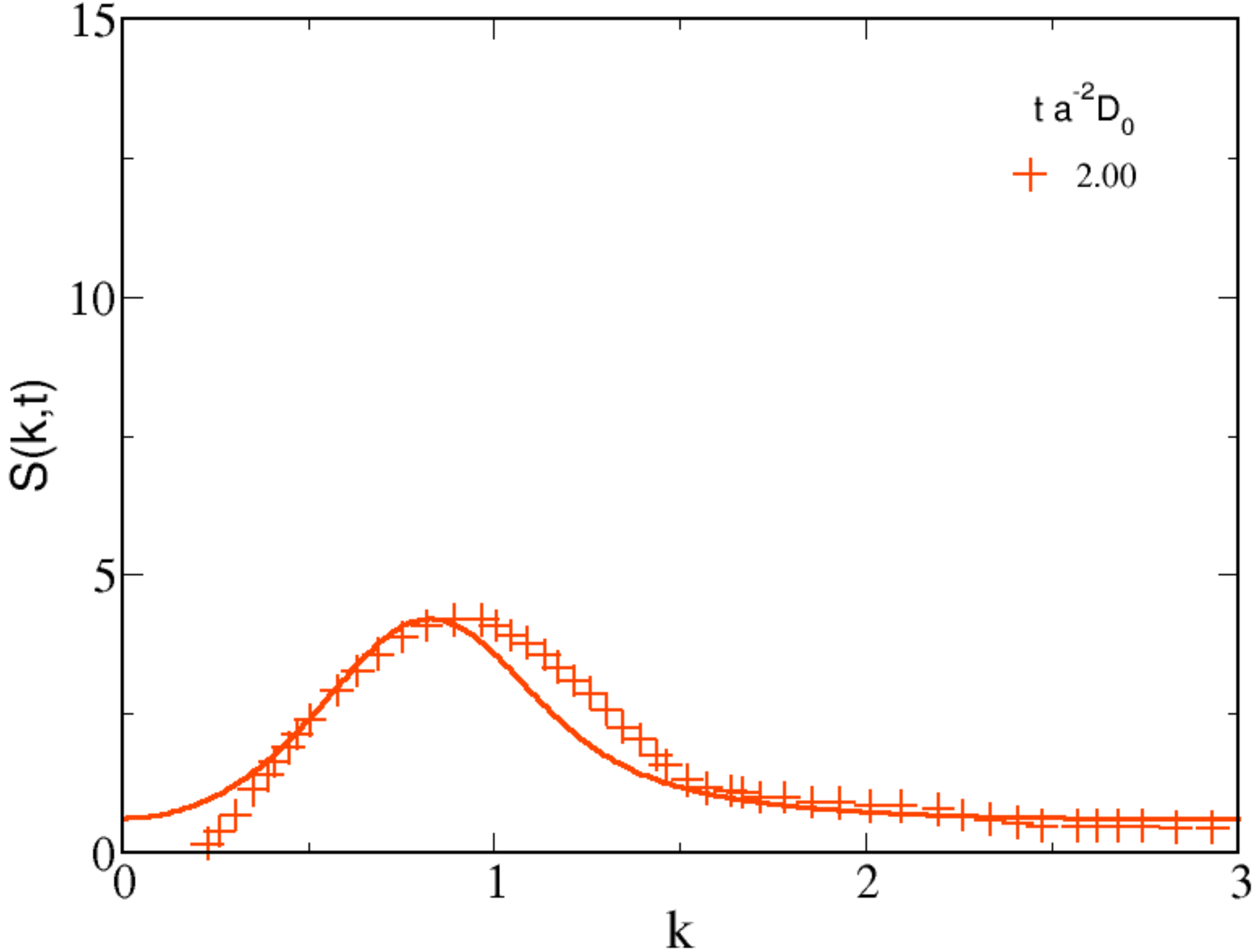
S(k,t)
k
t = 0.0
t = 0.8
t = 1.6
t = 2.4
t = 3.2
t = 4.0
t = 4.8
t = 5.6
t = 6.4
t = 7.2
t = 8.0
t = 8.8
t = 10
t = 50
t_a
(a)
S(k_max, t)
t
T=0.20
T=0.30
T=0.40
T=0.50
T=0.55
T=0.60
T=0.65
T=0.70
T=0.75
T



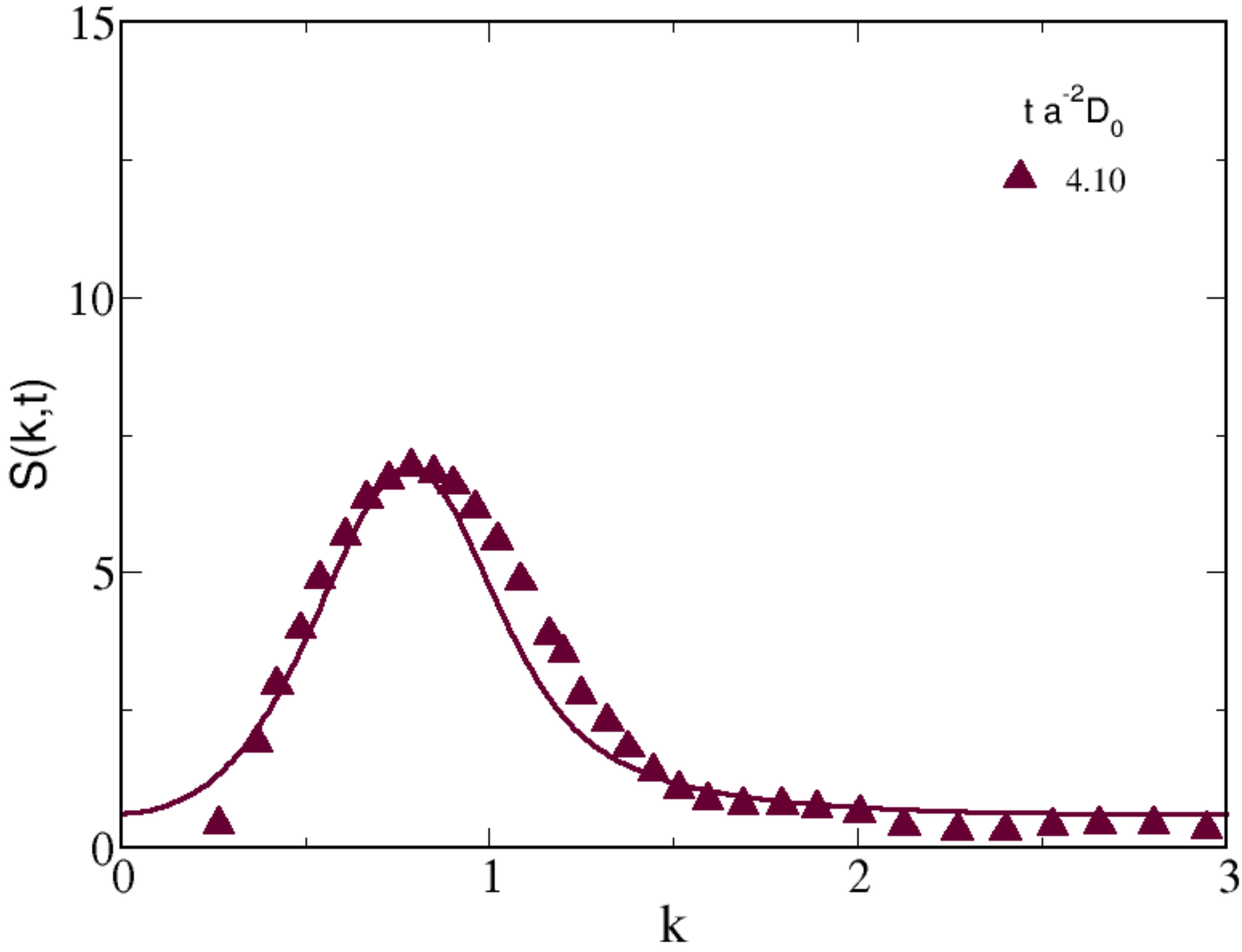
S(k,t)
k
t=0.0
t=0.8
t=1.6
t=2.4
t=3.2
t=4.0
t=4.8
t=5.6
t=6.4
t=7.2
t=8.0
t=8.8
ξ(t)
t
T
T=0.20
T=0.30
T=0.40
T=0.50
T=0.55
T=0.60
T=0.65
T=0.70
T=0.75
(b)



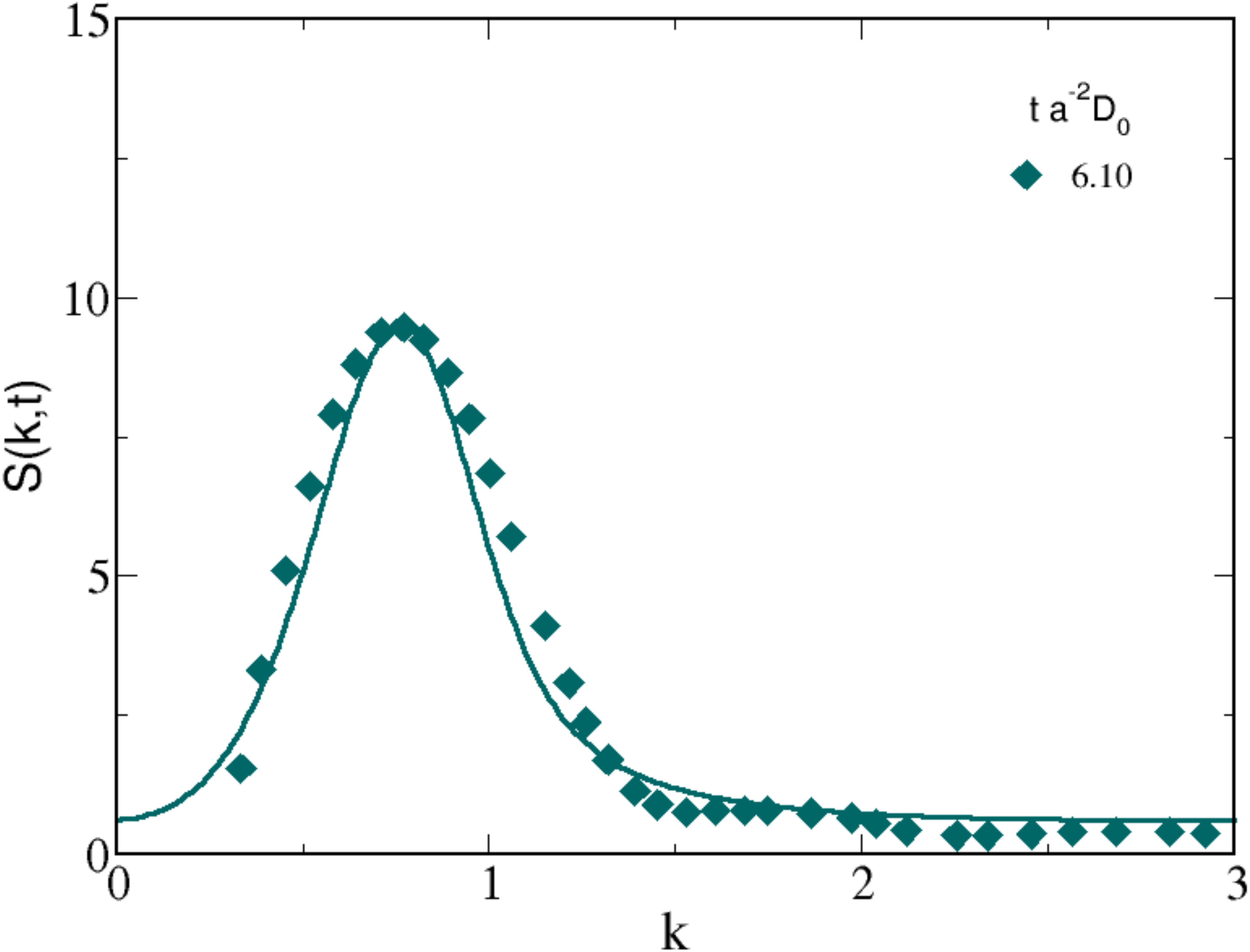
15
10
5
0
0
1
2
3
k
S(k,t)
t a^-2 D_0
0.40



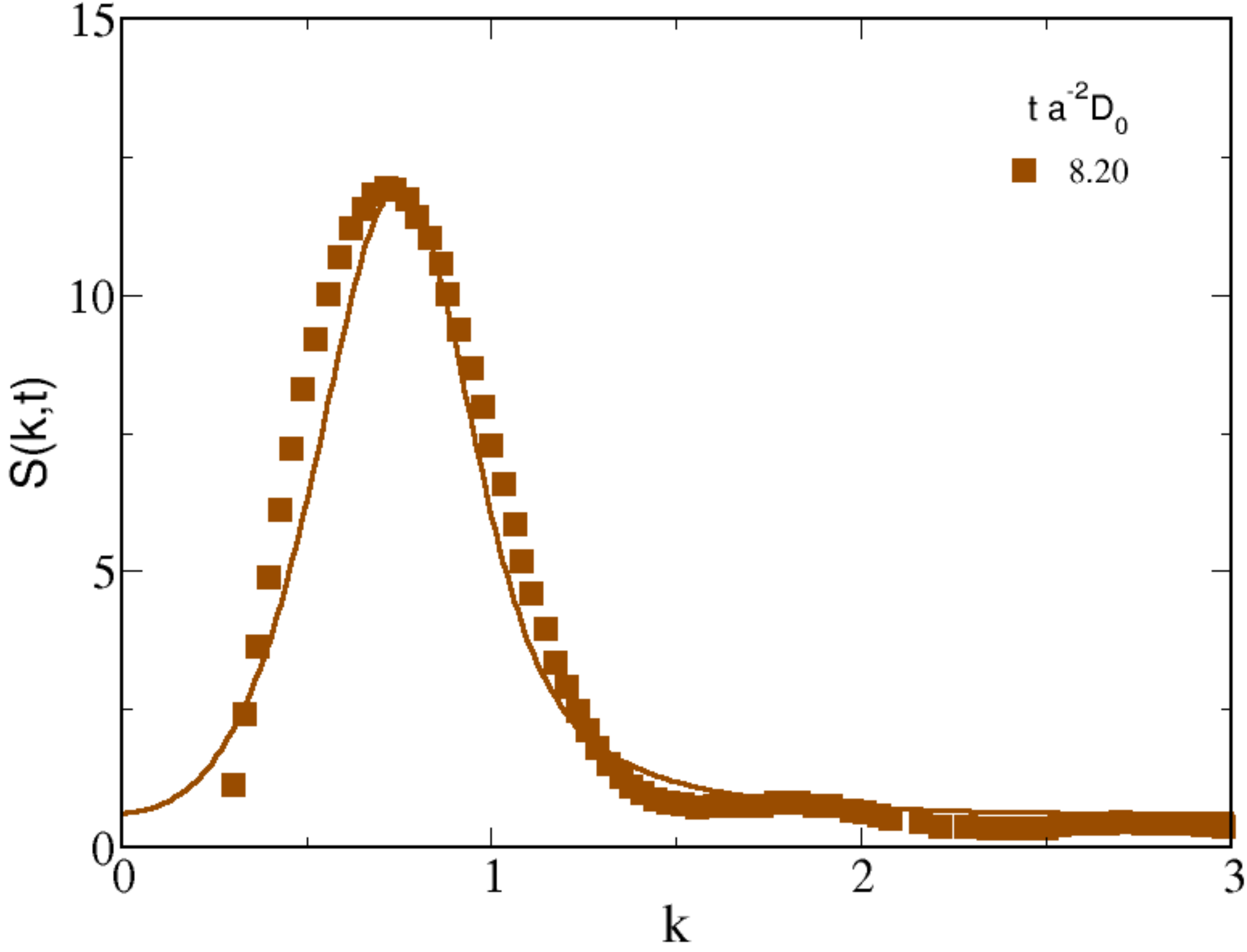
t a^-2 D_0
2.00
S(k,t)
k
0
5
10
15
1
2
3



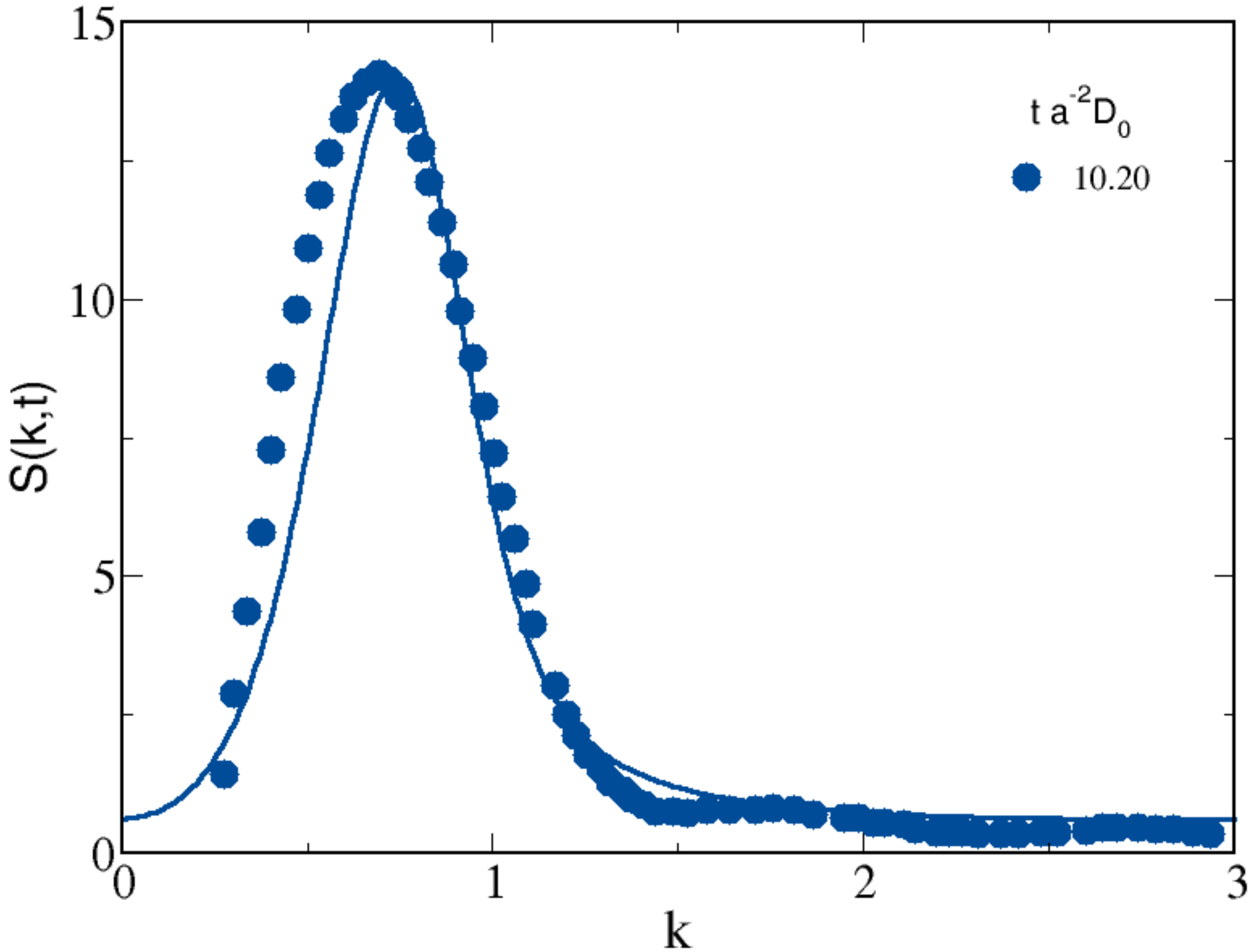
t a^-2 D_0
4.10
S(k,t)
k
0
5
10
15
1
2
3



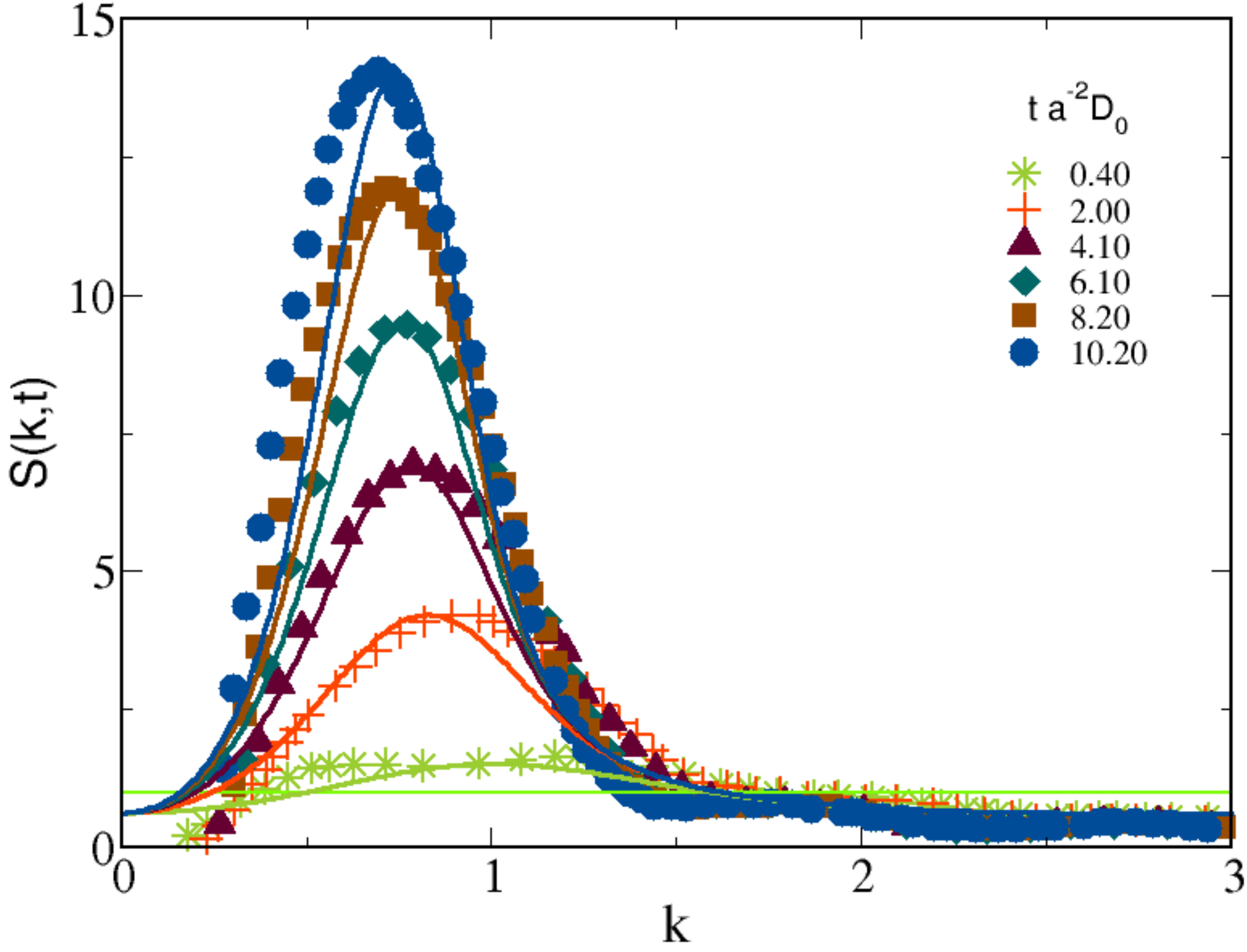
15
10
5
0
0
1
2
3
k
S(k,t)
t a^-2 D_0
6.10



15
10
5
0
0
1
2
3
k
S(k,t)
t a^-2 D_0
8.20



15
10
5
0
0
1
2
3
k
S(k,t)
t a^-2 D_0
10.20



15
10
5
0
S(k,t)
0
1
2
3
k
t a^-2 D_0
0.40
2.00
4.10
6.10
8.20
10.20

CONTENT

- Introduction and advanced summary.
- Fundamental principles: (molecular) thermodynamics.
- Fundamental principles: (molecular) Irreversible thermodynamics.
- *Equilibrium* Self-consistent generalized Langevin equation (SCGLE) theory.
- Aging and irreversibility: the NE-SCGLE theory.
- Full exercise: Lennard-Jones—like liquid.
- Perspectives.

Structural and Dynamical Heterogeneity

$$\frac{\partial \overline{n}(\mathbf{r},t)}{\partial t} = D^0 \nabla \cdot b(\mathbf{r},t) \overline{n}(\mathbf{r},t) \nabla \beta\mu[\mathbf{r};\overline{n}(t)]$$

$$\frac{\partial \sigma(k;\mathbf{r},t)}{\partial t} = -2k^2 D^0 \overline{n}(\mathbf{r},t) b(\mathbf{r},t) \mathcal{E}(k;\overline{n}(\mathbf{r},t)) \sigma(k;\mathbf{r},t) + 2k^2 D^0 \overline{n}(\mathbf{r},t)\ b(\mathbf{r},t),$$

Strategy: write

$$n(\mathbf{r},t) = n + \Delta n(\mathbf{r},t),$$

and start by neglecting

$$\Delta n(\mathbf{r},t)$$

Strategy: write

$$n(\mathbf{r},t) = n + \Delta n(\mathbf{r},t),$$

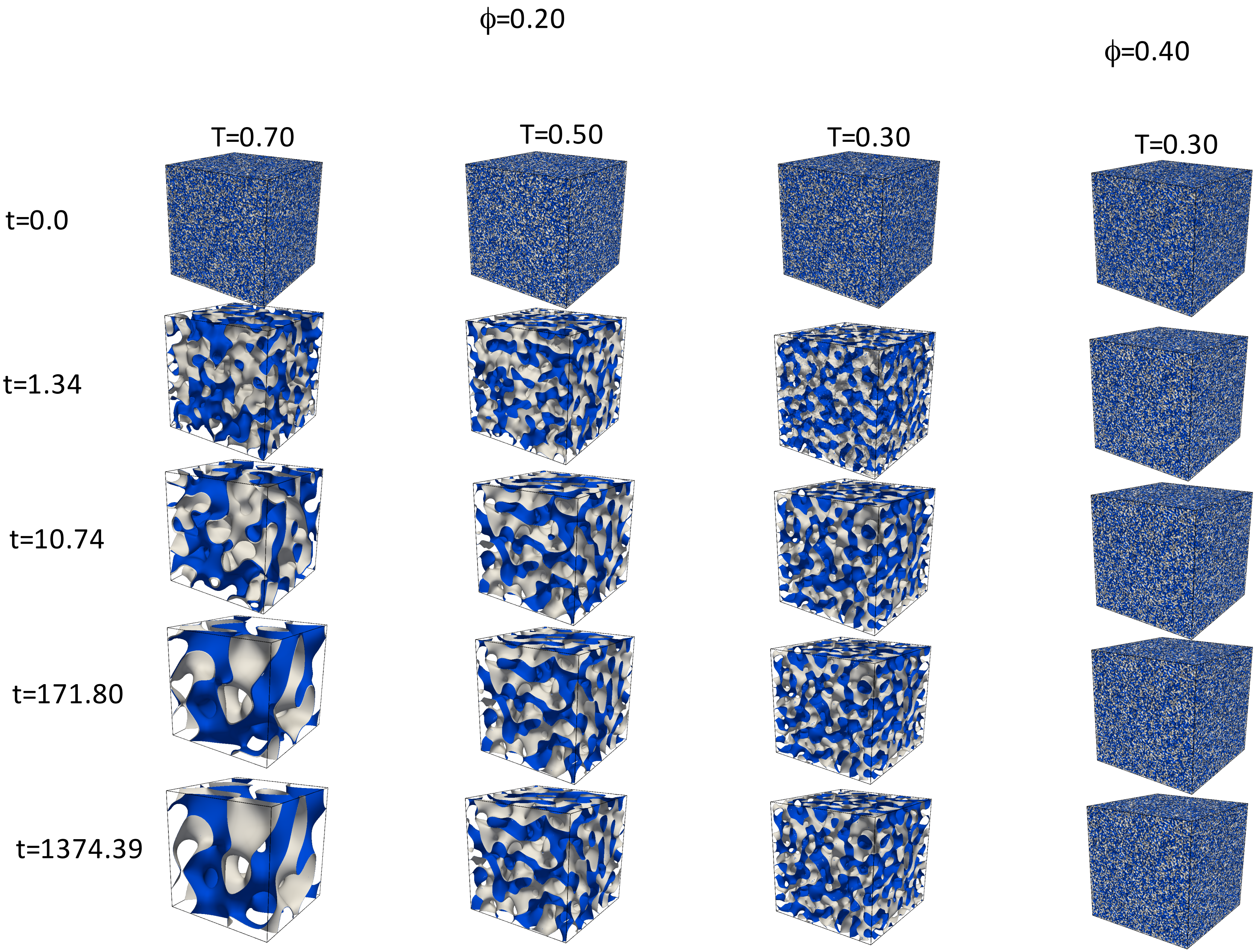
but now do not neglect

$\Delta n(\mathbf{r},t)$!....

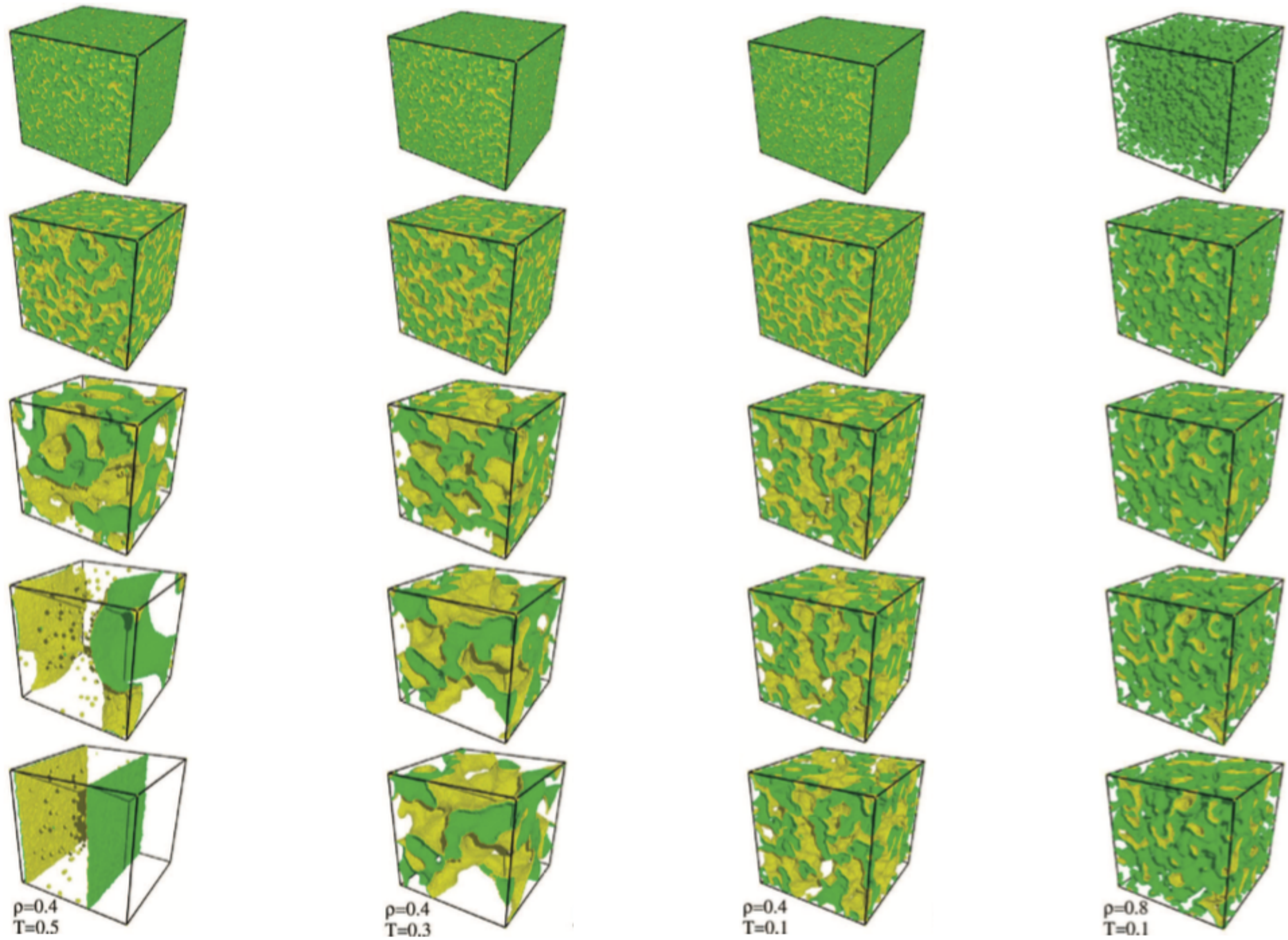
Instead, linearize this equation,

$$\frac{\partial \overline{n}(\mathbf{r},t)}{\partial t} = D^0 \nabla \cdot b(\mathbf{r},t) \overline{n}(\mathbf{r},t) \nabla \beta \mu [\mathbf{r}; \overline{n}(t)]$$

in $\Delta n(\mathbf{r},t)$



ϕ=0.20
ϕ=0.40
T=0.70
T=0.50
T=0.30
T=0.30
t=0.0
t=1.34
t=10.74
t=171.80
t=1374.39


ρ=0.4
T=0.5
ρ=0.4
T=0.3
ρ=0.4
T=0.1
ρ=0.8
T=0.1

Dipolar Janus Particles

(HS + Dipolar) Interaction

$$u(1,2) = u_{HS}(\mathbf{r}_{12}) + f(\mathbf{r}_{12})\, D(\mathbf{r}, \mu_1, \mu_2)$$

with

$$D(\hat{r}, \mu, \mu') = 3(\hat{r} \cdot \mu)(\hat{r} \cdot \mu') - (\mu \cdot \mu')$$

and $$f(r) = 1/r^3$$

(HS + Shoulder) Interaction

$$u(1,2) = u_{HS}(\mathbf{r}_{12}) + f(\mathbf{r}_{12})\, D(\mathbf{r}, \mu_1, \mu_2)$$

with

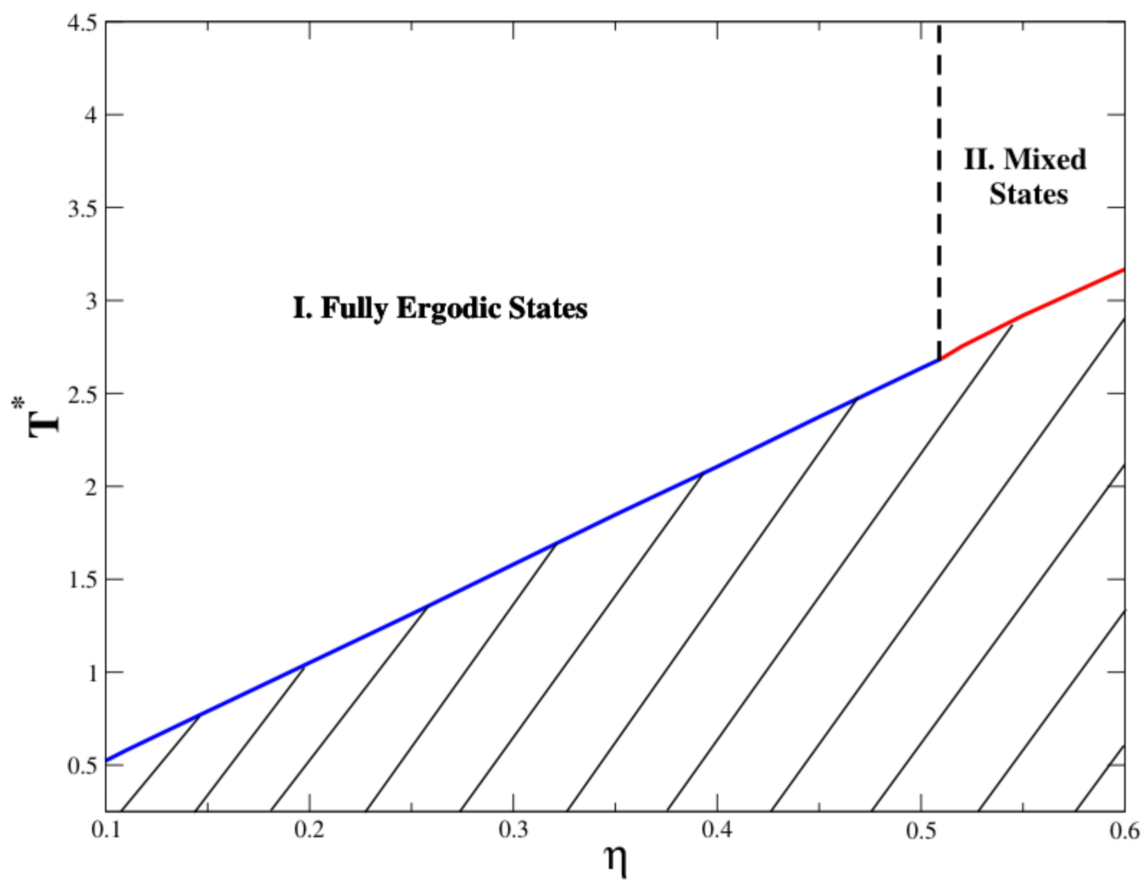
$$D(\hat{r}, \mu, \mu') = 3(\hat{r} \cdot \mu)(\hat{r} \cdot \mu') - (\mu \cdot \mu')$$

and

$$f(r) = e^{-zr}/r$$

Anisotropic interaction: Yukawa-like potential

Dynamical Arrest Diagram: Equilibrium vs. Non equilibrium SCGLE



(HS + Well) Interaction

$$u(1,2) = u_{HS}(\mathbf{r}_{12}) + f(\mathbf{r}_{12})\, D(\mathbf{r}, \mu_1, \mu_2)$$

with

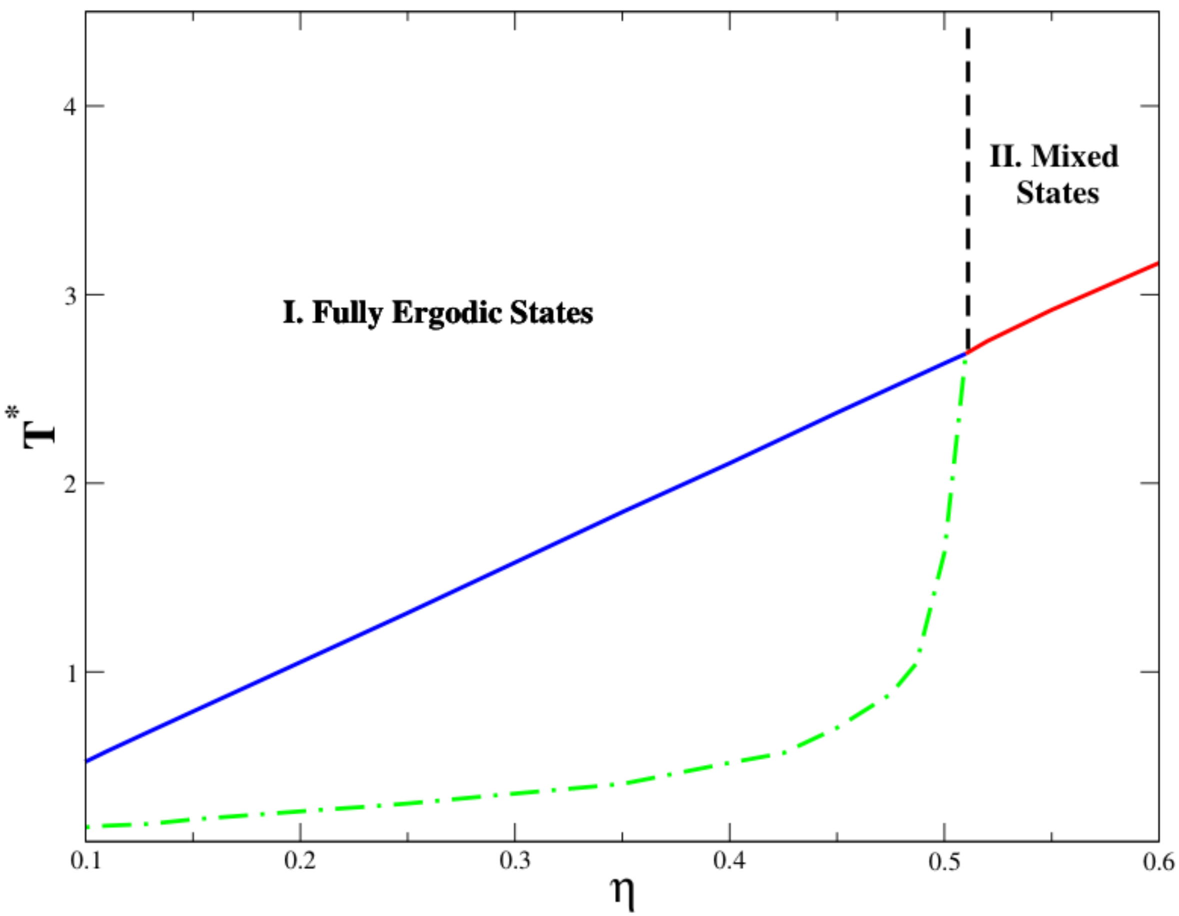
$$D(\hat{r}, \mu, \mu') = 3(\hat{r} \cdot \mu)(\hat{r} \cdot \mu') - (\mu \cdot \mu')$$

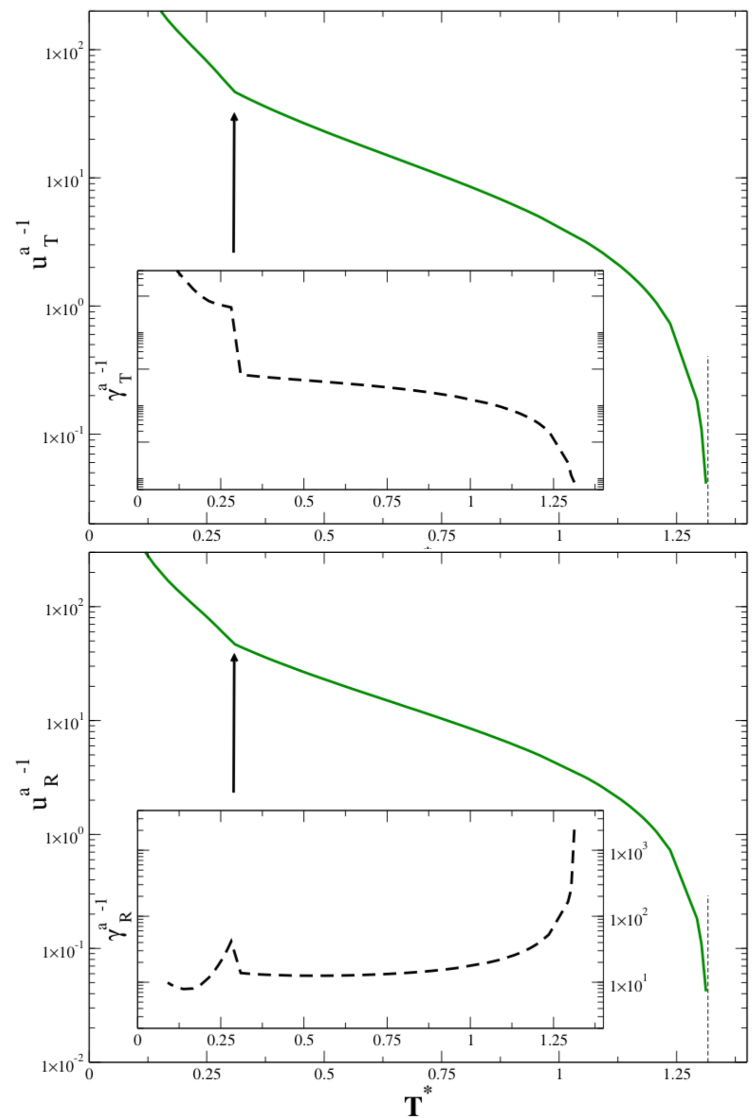
and

$$f(r) = -\, e^{-zr}/r$$

Anisotropic interaction: Yukawa-like potential

Dynamical Arrest Diagram: Equilibrium vs. Non equilibrium SCGLE





Soft matter group at Universidad Autónoma de San Luis Potosí

Pedro Ramírez-González

Lety López-Flores

Paty Mendoza-Méndez

José Manuel Olais-Govéa

Edilio Lázaro-Lázaro

Ernesto Cortés-Morales

J. Manuel Olais-Govea, Leticia López-Flores,

and

Martín Chávez-Páez

Instituto de Física 'Manuel Sandoval Vallarta',
Universidad Autónoma de San Luis Potosí, México

Agradecimientos: CONACyT, SEP, UASLP

CONCLUSIONS

- The NE-SCGLE theory describes non-equilibrium processes from first principles.
- It describes a number of relevant well-known and relevant signatures of the glass and gel transitions.
- It is flexible enough to be extended in various other directions (molecular systems, heterogeneous conditions, arbitrary non-equilibrium protocols, etc.)